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IDENTIFICATION OF REACTION INTERMEDIATES IN COMBUSTION REACTIONS INVOLVING HALOCARBON FLAME RETARDANTS.

by

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ABSTRACT

The pyrolysis of some perfluoro organic iodides have been used to prepare free radical species, of possible importance in flame inhibition chemistry, for infrared matrix isolation studies. The species CF_3O_2, C_2F_5, $n-C_3F_7$ and iso-C_3F_7 were identified and vibrational assignments made. For CF_3O_2, oxygen isotope studies were used to help in the vibrational assignments. Papers for publication have been prepared describing this work and are included in this report. Normal coordinate analyses for CF_3O_2 and C_2F_5 are currently in progress and will be submitted for publication in 1980. Preliminary data from these calculations strongly support the initial vibrational assignments made for CF_3O_2 and C_2F_5. Attempts were made to identify the species CF_3O, $t-C_4F_9$, C_6F_5 and $C_6F_5O_2$. Some evidence for the existence of CF_3O was found but was not definitive. The results of these latter studies are described in the first section of this report.
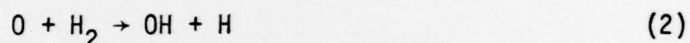
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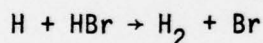Papers Submitted for Publication

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1. INTRODUCTION

It is well known that the addition of small amounts of certain materials (flame retardants) to combustion systems can have a marked inhibitory effect on the reactions. For obvious safety reasons, there has been much interest in these materials and considerable effort has been devoted to understanding the mechanism of flame inhibition. The generally accepted view is that these materials act as radical sinks in the chain branching reactions which are necessary for the propagation of combustion. Two important chain branching reactions in hydrocarbon combustion are[1]:

$$H + O_2 \rightarrow HO + O \tag{1}$$

$$O + H_2 \rightarrow OH + H \tag{2}$$

If HBr, a well known flame retardant, or some material capable of forming HBr in the precombustion zone is present, then the reaction,

$$H + HBr \rightarrow H_2 + Br$$

can compete with the chain branching reaction (1) above. Alternatively, if CF_3Br is present in the system as a fire retardant, then the reaction,

$$CF_3 \, Br + O \rightarrow products^{(2)}$$

is rapid enough to compete with the chain branching reaction, (2) above. That only a relatively small amount of the flame retardant is required suggests that its action is probably involved in the radical chain branching reaction.

Although the above picture of flame retardant action for halogen containing flame inhibitor is probably generally correct, in detail there are many unaswered questions. In the present instance attention is focused on halocarbon flame retardants. A listing of some of these materials is presented in Table 1 in decreasing order of effectiveness and it has been concluded that

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Table 1

SUMMARY OF COMPOUNDS EVALUATED AS FIRE EXTINGUISHING AGENTS FOR n-HEPTANE-AIR

ROOM TEMPERATURE, 300-500 mm Hg ABSOLUTE PRESSURE

Compound Formula	Compound Name	Peak in Flammability Curve, Vol %
CBr_2F_2	Dibromodifluoromethane	4.2
CBr_3F	Tribromofluoromethane	4.3
$CF_3CHBrCH_3$	2-Bromo-1,1,1-trifluoro-propane	4.9
$CBrF_2CBrF_2$	1,2-Dibromotetrafluoroethane	4.9
CF_2ICF_2I	Tetrafluoro-1,2-diiodoethane	5.0
CH_2Br_2	Dibromomethane	5.2
CF_3CF_2I	Pentafluoroiodoethane	5.3
$CF_3CH_2CH_2Br$	3-Bromo-1,1,1-trifluoropropane	5.4
CH_3CH_2I	Ethyliodide	5.6
CF_3CF_2Br	Bromopentafluoroethane	6.1
CH_3I	Methyl iodide	6.1
$CBrF_3$	Bromotrifluoromethane	6.1
CH_3CH_2Br	Ethyl bromide	6.2
$CH_2BrCF_2CH_3$	1-Bromo-2,2-difluoropropane	6.3
$CClF_2CHBrCH_3$	2-Bromo-1-chloro-1,1-difluoro-propane	6.4
$CHBr_2F$	Dibromofluoromethane	6.4
$CBrF_2CH_2Br$	1,2-Dibromo-1,1-difluoroethane	6.8
CF_3CH_2Br	2-Bromo-1,1,1-trifluoroethane	6.8
$C_6F_{11}C_2F_5$	Perfluoro(ethylcyclohexane)	6.8
$1,3-C_6F_{10}(CF_3)_2$	Perfluoro(1,3-dimethylcyclohexane)	6.8
$1,4-C_6F_{10}(CF_3)_2$	Perfluoro(1,4-dimethylcyclohexane)	6.8
CF_3I	Trifluoroiodomethane	6.8
CH_2BrCH_2Cl	1-Bromo-2-chloroethane	7.2
$CClF\ CH\ Br$	2-Bromo-1-Chloro-1,1-difluoro-ethane	7.2
$C_6F_{11}CF_3$	Perfluoro(methylcyclohexane)	7.5
C_7F_{16}	Perfluoroheptane	7.5
CH_2BrCl	Bromochloromethane	7.5
$CHBrF_2$	Bromodifluoromethane	8.4
$CClF_2CCl_2F$	1,1,2-trichlorotrifluoroethane	9.0
$CBrClF_2$	Bromochlorodifluoromethane	9.3
HBr	Hydrogen bromide	9.3
CH_3Br	Methyl bromide	9.7
CF_2-CHBr	2,2-Difluorovinyl bromide	9.7
C_4F_{10}	Perfluorobutane	9.8
$SiCl_4$	Silicon tetrachloride	9.9

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Table 1 (Continued)

Compound Formula	Compound Name	Peak in Flammability Curve Vol %
$CBrF_2CBrClF$	1,2-Dibromo-2-chloro-1,1,2-trifluoroethane	10.8
$CClF_2CClF_2$	1,2-dichlorotetrafluoroethane	*10.8
CCl_4	Carbon tetrachloride	11.5
$CF_3CHClCH_3$	2-chloro-1,1,1-trifluoropropane	12.0
$CF_3CH_2CH_2Cl$	3-chloro-1,1,1-trifluoropropane	12.2
$CClF_3$	Chlorotrifluoromethane	12.3
CF_3CF_3	Hexafluoroethane	13.4
CCl_2F_2	Dichlorodifluoromethane	14.9
$CHCl_3$	Chloroform	17.5
CHF_3	Trifluoromethane	17.8
$CHClF_2$	Chlorodifluoromethane	17.9
C_4F_8	Octafluorocyclobutane	18.1
SF_6	Sulfur hexafluoride	20.5
BF_3	Boron trifluoride	20.5
PCl_3	Phosphorus trichloride	22.5
HCl	Hydrogen chloride	25.5
CF_4	Carbon tetrafluoride	26
CO_2	Carbon dioxide	29.5
H_2O	Water	>8
$(C_2F_5)_2NC_3F_7$	Heptadecafluoro(N,N-diethyl-propylamine	>8.5
CH_2Cl_2	Dichloromethane	·11

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the efficiency of a given halogen containing fire retardant follows the order $I > Br > Cl > F$.

For practical reasons, iodine compounds are not usually used, they undergo decomposition too easily on storage. Mostly, chlorine and bromine compounds are used and their mode of action is usually attributed to the ready release of bromine and chlorine with the formation of HBr and HCl. The latter can act as good H atom scavengers and the element Br_2 or Cl_2 can remove radicals such as CH_3 with the formation of CH_3Br^2.

In one article[3] the author dismissed fluorine compounds as possible flame retardants since the CF bond is so strong that it (presumably fluorine) cannot serve as a radical trap. It is indeed true that the CF bond is extremely stable and that the H atom reaction sink mechanism,

$$H + HF \rightarrow H_2 + F$$

will not occur (cf HBr and HCl) since the energetics are not favorable. However, in Table 1 it will be observed that the completely fluorinated species $C_6F_{11}C_2F_5$, 1:3 $C_8F_{10}(CF_3)_2$, 1:4 $C_6F_{10}(CF_3)_2$, $C_6F_{11}CF_3$ and C_7F_{16} are better fire retardants than many chlorine and bromine containing compounds, including HBr and HCl.

It is clear that the mode of action of these completely fluorinated compounds as fire retardants cannot be the same as those containing chlorine and bromine. The fact that C_2F_5I is markedly more effective than CF_3I is also evidence that the fluorine moiety in the molecule is of importance since the C-I bond dissociation energies for both compounds only differ by about 4 percent. In one study using a mass spectrometer to sample a diffusion flame containing CF_3Br^5, CF_3 could not be detected, presumably because of its low concentration, though it was suggested that it probably played an important role in the fire retarding action but exactly what, was not clear.

In essence, the above briefly summarizes the state of knowledge on the details of halocarbon fire retardant action at the time the present study was initiated. Since it appeared likely that perfluoro radicals might play an important role in flame retardancy, the present study was initiated to characterize some perfluoro halocarbon free radicals and their possible

oxidation products using matrix isolation IR spectroscopy. It was hoped that the radical species shown in Table 2 could be generated and characterized. Essentially, complete success was obtained for items 1, 3, 5 and 6 and the results from these studies are included in this report in the form of papers submitted for publication. For items 2, 4, 7, 8 and 9 either the desired result was not obtained, or the data defied interpretation, or insufficient time was available to obtain all the experimental data required to make a complete analyses. The results of the studies concerning items 2, 4, 7, 8 and 9 will be briefly presented.

2. RESULTS

2a. Matrix Studies to Identify CF_3O

The pyrolyses of CF_3OF and CF_3OOCF_3 were both tried as potential sources of CF_3O. Experiments with CF_3OF only resulted in the formation of COF_2 and possibly a little CF_4 and no other products as identified from the IR spectra. The pyrolysis of CF_3OOCF_3 gave results which were somewhat more encouraging. Mixtures of CF_3OOCF_3 in argon ranging from 0.05-0.30 percent were pyrolyed in the plantinum effusion tube at temperatures from 300-600°C. Flow rates for the Ar + $(CF_3)_2O_2$ mixture and the argon matrix were similar to those used in the $CF_3I + O_2$ experiments. Very little decomposition of the parent compound was observed unless the pyrolysis temperature was above 450°C.

It soon became apparent that the pyrolysis of the peroxide was dependent on the pyrolysis surface. The best results were obtained after conditioning the platinum pyrolysis tube at ~700°C with a slow flow of C_6F_5I. Some success was also obtained using pyrex and LiF lined pyrolysis tubes without conditioning with C_6F_5I. Unknown absorption bands occurred at 1276 and 1234 cm^{-1}. COF_2 was always the major product and overlapped partially the 1234 cm^{-1} feature. Other minor products identified were CF_4, C_2F_6, CF_3, CF_2 and C_2F_4. Several unidentified weak bands were observed in the region 600-1200 cm^{-1} but did not correlate with the two features at 1276 and 1234 cm^{-1}. Because the major decomposition product was COF_2 it was not possible to build up very high concentrations of the species responsible for the 1276 and 1234 cm^{-1} features.

Table 2

PERFLUOROHALOCARBON RADICAL SPECIES SOUGHT AND METHOD
OF PREPARATION FOR MATRIX STUDIES

Radical

1. CF_3O_2 — Pyrolysis of CF_3I or CF_3Br and subsequent reaction of CF_3 with an O_2 doped matrix

2. CF_3O — Pyrolysis of CF_3OF and $CF_3O_2CF_3$

3. C_2F_5 — Pyrolysis of C_2F_5I

4. $C_2F_5O_2$ — Pyrolysis of C_2F_5I and subsequent reaction of C_2F_5 with an O_2 doped matrix

5. $n-C_3F_7$ — Pyrolysis of $n-C_3F_7I$

6. $iso-C_3F_7$ — Pyrolysis of $iso-C_3F_7I$

7. $t-C_4F_9$ — Pyrolysis of $t-C_4F_9I$

8. C_6F_5 — Pyrolysis of C_6F_5I

9. $C_6F_5O_2$ — Pyrolysis of C_6F_5I and subsequent reaction of C_6F_5 with an O_2 doped matrix

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The appearance of only two absorption bands in the 1100-1300 cm^{-1} region, where C-F stretching vibrations occur with good absorption intensity, would be consistent with their assignment to a species CF_3O for which only two C-F stretching modes would be expected on the assumption of C_{3v} symmetry. If this assignment is correct, the failure to observe the four other IR active frequencies would simply infer that they have low absorption coefficients and our inability to build up large concentrations of the unknown compound precluded their detection.

It is possible that if more time had been available to search for a more unreactive pyrolysis surface, a more definitive conclusion could be obtained from the pyrolysis of CF_3OOCF_3.

2b. <u>Matrix Studies to Identify $C_2F_5O_2$</u>

An attempt was made to identify the species $C_2F_5O_2$ by pyrolying C_2F_5I to form the radical C_2F_5, and allowing the latter to react with an argon matrix containing oxygen during matrix deposition. The experimental conditions used were a composite of those given in the appendix for the identification of C_2F_5 and CF_3O_2. Oxygen isotope studies were made with O_2^{16}, O_2^{18} and $O^{16}O^{18}$.

Typical spectra of the 1350-900 cm^{-1} region are shown in Figure 1. The dotted curves are the spectra obtained at short deposition times, and the full line curves the analogous spectra at somewhat longer deposition times. In the spectra the various known chemical species are identified and new unknown absorption bands indicated with question marks. It is at once apparent from these spectra that absorption band overlapping was particularly severe in these experiments, and in fact it was impossible to make any really definitive assignments for the unknown absorption bands. A careful search was made for an O-O type stretching frequency in the 1000-1100 cm^{-1} region showing an isotope shift, $\nu(O_2^{16})/\nu(O_2^{16})$ of about 1.05 as found in CF_3O_2. No such frequencies could be clearly identified, though unquestionably bands which showed frequency shifts on O_2^{16} and O_2^{18} isotopic substitution could be easily identified. With the mixed O_2^{16}, $O^{16}O^{18}$ and O_2^{18} isotopes a triad of bands at about 1041, 1028 and 1016 cm^{-1} was tentatively identified which could conceivably be assigned to a C-O stretching vibration. If indeed this assignment were correct, and the species responsible, $C_2F_5O_2$, then it would require

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Transmittance (Percent)

Frequency (Cm⁻¹)

1300   1200   1100   1000   900

Fig. I MATRIX ISOLATION SPECTRA OF PYROLYSIS PRODUCTS OF
C₂F₅I IN 10% ¹⁶O₂ + 90% Ar (top), 10% ¹⁸O₂ + 90% Ar (middle)
AND 10% (¹⁸O₂ + ¹⁸O¹⁶O + ¹⁶O₂) + 90% Ar (bottom)

that the C-O stretch in this radical is almost 200 cm^{-1} larger than in CF_3O_2. Indeed the C-O stretching force constant in CF_3O_2 is rather small by comparison with other C-O stretching frequencies, so a larger value in $C_2F_5O_2$ is perhaps not unreasonable.

In the CF_3O_2 system, fairly substantial amounts of COF_2 were formed. CF_3CFO, perfluoroacetyl fluoride, an analogous product which might possibly be expected in the $C_2F_5 + O_2$ system was not found.

As noted earlier no absorption bands corresponding to an expected O-O stretch could be identified. This should not be taken as evidence that $C_2F_5O_2$ was not present in the matrix since the O-O stretching mode could simply be overlapped with absorption bands from other species. That CF_3O_2 readily forms by the interaction of CF_3 with O_2 strongly suggests that the analogous compound $C_2F_5O_2$ also exists. It seems highly probable that if the capabilities of the more modern IR spectrometers were used to study this system, computer aided spectral subtraction techniques would enable interpretation of the spectra to be made.

2c. Matrix Studies to Identify $t\text{-}C_4F_9$

With the same procedures as used in the formation of CF_3, C_2F_5, $n\text{-}C_3F_7$ and iso C_3F_7 a sample of $t\text{-}C_4F_7I$ was pyrolysed at $\approx 550°C$, a temperature at which the former perfluoroiodides showed substantial decomposition, and the products isolated. The IR spectrum clearly showed that essentially all the $t\text{-}C_4F_9I$ was destroyed and a single new product perfluoro-2-methyl propene formed. The pyrolysis temperature was progressively lowered until at 300°C about the same fraction of the iodide was decomposed (40-60%) as with the lower perfluoro alkyl iodides at 550°C. In experiments with relative short deposition times only $t\text{-}C_4F_9I$ and the propene C_4F_8 were identified as the pyrolysis products. However, at long deposition times a weak band at 603 cm^{-1} began to grow-in which could not be assigned to either of the above species.

In view of the markedly different pyrolysis behavior of $t\text{-}C_4F_9I$ compared to that of the lower perfluoroakyl iodides it appears possible that the primary bond breaking process may not be the same in the former as in the latter. Recent measurements[4] (have shown the following C-I bond energies in CF_3I (52.6 k cal mol^{-1}),

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C_2F_5I(50.6 k cal mol^{-1}), n-C_3F_7I(49.2 k cal mol^{-1}) iso-C_3F_7I(49.2 k cal mol^{-1}) and n-C_4F_9I(48.4 k cal mol^{-1}). These values are a little lower (3-5)k cal mol^{-1} than found in the corresponding hydrogen substituted compounds. The C-I bond energy in t-C_4F_9I is not known; the corresponding value in t-C_4H_9I is 55.7 k cal mol^{-1} suggesting a value of $\simeq 52 \pm 3$ k cal mol^{-1} for the perfluoroiodide. Under the low pressure pyrolysis conditions used in the present study, a C-I bond energy of this magnitude would require a temperature of $\simeq 500$-$600°C$ to affect substantial decomposition assuming C-I bond fission is the primary process and that the pre-experimental factor for the reaction is approximately the same as in the lower homologues, as would be expected. The low pyrolysis temperature of $300°C$ thus appears to imply a C-I bond energy in t-C_4F_9I of $\simeq 35$ k cal mol^{-1}, a value which seems much too low compared to the estimated value of $\simeq 52$ k cal mol^{-1}. These conflicting data may be reconciled if the primary bond breaking process in t-C_4F_9I is not C-I bond fission, but rather a concerted elimination reaction in which a four centered complex is formed with the elimination of 1F. This type of reaction is well known in some alkyl halide pyrolyses in which HX is eliminated from four a centre reaction complex resulting in an activation energy markedly lower than that corresponding to the C-X bond breaking energy, if that were the primary process. Some further evidence in support of such behavior may be inferred from the appearance of a weak absorption band which grew in slowly at 603 cm^{-1}. In the gas phase, IF has a fundamental vibration frequency of 604 cm^{-1}, and the 603 cm^{-1} matrix band could well be due to this specie which a concerted complex fission process would require to be formed. It is possible that IF could be formed by reaction between F atom and I atoms in the matrix due to poor isolation; the F atoms arising from the reaction t-$C_4F_9 \rightarrow C_4F_8$ + F. To eliminate this possibility, t-C_4F_9I was pyrolysed into argon matrices containing 5 percent CO and 5 percent O_2, respectively. Experience has shown in this laboratory and elsewhere that F atoms will react with CO and O_2 under our experimental conditions to produce FCO and FO_2. In neither case was any evidence found for FCO or FO_2 formation and the absorption feature attributed to FI at 603 cm^{-1} was unaffected.

In conclusion the above evidence strongly suggests that the pyrolysis of t-C_4F_7I at $\rightarrow$ 570K occurs via a complex four centered elimination reaction

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with the formation of perfluoro-2-methyl-propene and IF rather than simple fission of the C-I bond as appears to be the mechanism in pyrolysis of the lower perfluoro-alkyl iodides.

2d. Matrix Studies to Identify C_6F_5 and $C_6F_5O_2$

The pyrolysis of C_6F_5I required temperatures of 1000-1100K to obtain substantial decomposition, some 100-200K higher than in the C_1-C_3 perfluoro iodides, a finding consistent with C-I bond dissociation in C_6F_5I at 277 kJ mol^{-1}[6]. This latter value was determined using the toluene carrier gas technique. The presence of the C_6F_5 radical in the system was inferred from the formation of C_6F_5H by H abstraction from the toluene carrier gas. In the matrix study the only products found on pyrolysis of C_6F_5I were unreacted C_6F_5I, CF_4, CF_3, and CF_2 in approximately equal amounts. No evidence of absorption features attributable to any other species was found. These results imply a complete breakdown of the benzenoid ring structure on pyrolysis. When the pyrolysis products were trapped in an argon matrix containing 5 percent O_2, CF_3O_2 [7] was immediately recognizable in the product spectrum. No FO_2 was found, indicating the absence of free F-atoms in the pyrolysis reaction; nor was there any trace of COF_2, invariably found when CF_3, formed by the pyrolysis of CF_3I, was allowed to react with an oxygen-doped matrix in an earlier study [7]. Substantial amounts of CO and CO_2 were found; whether their formation occurred in the pyrolysis tube (by possible diffusion of O_2 into the pyrolysis zone) or by reaction of some carbon fragment in the matrix was not clear.

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PAPERS SUBMITTED FOR PUBLICATION

1. IR Matrix Isolation Spectra of Some Perfluoro Organic-Free Radicals
    Part 1, C_2F_5, Accepted for publication J. Fluorine Chemistry.

2. IR Matrix Isolation Spectra of Some Perfluoro Organic-Free Radicals
    Part 2, CF_3O_2, Accepted for publication J. Phys. Chem., December 1979.

3. IR Matrix Isolation Spectra of Some Perfluoro Organic-Free Radicals
    Part 3, $n\text{-}C_3F_7$ and iso-C_3F_7, submitted for publication J. Fluorine Chemistry.

4. IR Matrix Isolation Product Characterization from Low-Pressure Pyrolysis
    of $C_nF_{2n+1}I$ (n = 1-4) and C_6F_5I, submitted for publication to J. Fluorine
    Chemistry.

IR MATRIX ISOLATION SPECTRA OF SOME PERFLUORO ORGANIC-FREE RADICALS
PART 1. C_2F_5

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SUMMARY

The pentafluoro ethyl radical has been prepared by the pyrolysis of
C_2F_5I in a platinum effusion tube at $\approx 650°C$ and isolated in an argon matrix.
By elimination of absorption bands attributable to known fluorine compounds
and from relative intensity measurements on the remaining bands, twenty
frequencies were assigned C_2F_5 in the spectral range 4000-200 cm^{-1}. Four-
teen of these frequencies were assigned as fundamentals of C_2F_5, with C_s
symmetry, and the remainder to combination or overtone modes of the radical.

INTRODUCTION

The matrix isolation technique in conjunction with a variety of
spectroscopic methods is now widely used for studying organic-free radical
species [1]. In the majority of past studies free radicals have been gener-
ated by photolysis of suitable precursors in situ in the matrix, after, or
during its deposition. Alternatively chemical abstraction reactions during
the deposition process have been widely used [2]. The generation of radi-
cals in molecular beams by pyrolysis of suitable precursors, with subse-
quent isolation in matrices, has, by comparison with the above approaches,
rarely been used.

Some years ago in this laboratory the pyrolyses of CH_3I, $(CH_3)_2Hg$ [3],
CF_3I, and C_2F_4 [4] were used to generate the radicals CH_3, CF_3, and CF_2,
respectively, for subsequent trapping in neon matrices. The three IR active
frequences of CH_3 were first identified in these studies as a subsequent
investigation verified [5]. Despite this success of the pyrolysis approach,
few other workers tried the technique. Possibly the rather complex appear-
ance of the resulting spectra, due to the presence of a variety of stable

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and unstable products formed either in the pyrolysis, or by subsequent reaction in the matrix, detered other workers.

Recently we have had the opportunity to retry the pyrolsis generation of free radicals for IR matrix isolation studies. Perfluoro radicals have been investigated exclusively. In general, these species are considerably more stable than their hydrogenated analogues and this may have contributed in some measure to the success of the present studies. Much cleaner spectra have been obtained than reported in our earlier studies [3,4]. In this paper we present data on the IR spectrum of C_2F_5 formed via the pyrolysis of C_2F_5I.

EXPERIMENTAL

The experimental arrangement used in the present studies was very similar to that reported earlier [3,4], but with some variations which will be outlined. The liquid helium cold finger was replaced with an Air Products CS202 Displex closed cycle refrigerator capable of temperatures at the cold finger of 10-11 K. A platinum pyrolysis tube similar in dimensions to that used previously was inductively heated. The end of the tube closest to the matrix window was not attached to a water-cooled plate as required in the earlier configuration when resistance heating was used, but remained free. To minimize radiation from the pyrolysis tube reaching the matrix window, a water-cooled baffle with suitable skimmer orifice was interposed. Temperatures could be measured with an optical pyrometer. The pyrolysis temperatures were much lower than in the previous study ($\approx 1300°C$) [3,4], and in practice, the temperature was fixed by setting the current output of the rf. generator at a given value. It is estimated that pyrolysis temperatures were in the range 600-700°C.

C_2F_5I was stored in a 1-liter flask and its flow into the pyrolysis reactor controlled by a Granville Phillips all stainless steel leak valve. The low pressure side of the variable leak valve was monitored by an MKS Baratron capacitance pressure gauge. The C_2F_5I was leaked into the pyrolysis tube at rates of 8×10^{-7} to 4×10^{-5} moles hr^{-1}. From the geometry of the system, it was estimated that between 1-10% of the effusate reached the cooled window. Argon was used as a matrix gas in all experiments being bled in at $(2-4.5) \times 10^{-3}$ mole hr^{-1}. Matrices were deposited over periods of time ranging from 2-30 hrs. Spectra were recorded on a Perkin Elmer 621 spectrophotometer. Reported frequencies are believed accurate to ±1 cm^{-1} in the 2000-200 cm^{-1} region examined.

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MATERIALS

Linde Ultra High Purity Grade argon was used for the matrix gas. The following halocarbons--CF_4, C_2F_4, C_2F_6, C_3F_6, $n-C_4F_8$, and C_2F_5I--were obtained either from Matheson or Peninsular Research Chemicals, Inc. Stated purities ranged from 97 to 99.7%. All these materials were subjected to trap-to-trap distillation at liquid nitrogen temperature prior to use.

RESULTS AND DISCUSSION

The general experimental approach used in the present study was first to obtain matrix spectra of C_2F_5I and its possible stable pyrolysis products (the fluorocarbons listed above); second, to obtain matrix spectra of products from the C_2F_5I pyrolysis; third, to identify known stable and unstable halocarbons (CF_2 and CF_3) in the resulting spectra; and fourth, to make relative intensity measurements on the remaining unknown absorption bands to identify common precursor species.

The pyrolysis of C_2F_5I is expected to result in the scission of the C_2F_5-I bond (C—I bond energy = 220 ±4 kJ mol^{-1}) [6]. In preliminary experiments, various pyrolysis temperatures were tried, from approximately 600°C up to about 750°C. At the lower temperature very little pyrolysis occurred, whereas at the higher temperature, decomposition of the C_2F_5I was extensive, with formation of quite large amounts of CF_3 and CF_2, in addition to other unknown species being recognized easily from the spectra. The pyrolysis temperature used in the final experiments was a compromise between maximizing C_2F_5I decomposition and minimizing CF_3 and CF_2 formation; this temperature, as noted earlier, was in the range 600-750°C, resulting in approximately 20-40% decomposition of the C_2F_5I.

Under the optimum experimental conditions used in most of this study, the pyrolysis of C_2F_5I resulted in matrix spectra, which, from a cursory examination, appeared to consist of only two major components, unreacted C_2F_5I and a second unknown compound. Weak absorption bands attributable to CF_4, CF_3, CF_2, CF_3I, and possibly C_2F_4 were usually identifiable in the spectra, increasing in intensity somewhat at the higher pyrolysis temperatures. No positive identification of absorption bands attributable to C_2F_6, C_3F_6, C_3F_8, or $n-C_4F_{10}$ was ever made in a total of some 25 pyrolysis experiments.

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In organic fluorine compounds, carbon-fluorine stretching modes usually occur with strong absorption intensities while the bending modes are typically some one to two orders of magnitude weaker [7]. Because of this, characteristic matrix deposition times of 1-2 hrs sufficed to obtain moderate absorption band intensities for the C—F stretching modes in the 1400-1050 cm^{-1} region, whereas up to 30 hrs deposition time was required to obtain moderate, and in some cases still quite weak intensities, for the lower frequency bending modes.

As noted above, C_2F_5I was a major species present in all the pyrolysis spectra and for this reason several reference spectra of this compound were obtained at low and high intensity for comparison purposes. At moderate and high optical densities, the C_2F_5I spectra contained numerous absorption bands, and the spectra were carefully compared with those in the literature [8]. A total of some 34 overtone and combination bands were identified in the 2000-200 cm^{-1} region which had not previously been reported. They could all be accounted for in terms of the originally assigned fundamental modes [8] of C_2F_5I. These data are not included here since they in no way alter the earlier vibrational assignment for the molecule.

In Figures 1, 2, 3, and 4 the spectra of C_2F_5I pyrolysis products in the region of interest are presented. Spectra were carefully examined at short, medium, and long deposition times with comparable spectra (similar optical density) of C_2F_5I and the other fluorine species noted above. Absorption features attributable to known molecular species were assigned, leaving a total of some 20 absorption bands for which obvious assignment to known species was not possible.

Optical densities for these 20 absorption bands were measured and are shown in Table 1. The omissions in the table are due to the particular absorption feature being too weak or too strong for meaningful measurement. Absorption bands at 703 and 604 cm^{-1} were chosen as reference features and the relative intensities of all the other unknown absorption bands with respect to these two were calculated. The band at 703 cm^{-1} was selected since it was of medium intensity and could potentially provide a good reference, both for the stronger stretching modes in the higher frequency regions and the weaker bending modes at lower frequencies. Unfortunately, this band overlapped the ν_2 frequency of CF_3 at 701 cm^{-1}. The latter is one of the weaker bands of CF_3, but since the amount of CF_3, which was generally small, varied somewhat from experiment to experiment, due to the rather imprecise temperature control, its value as a reference band was in some measure

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Fig. 1 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

Fig. 2 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)
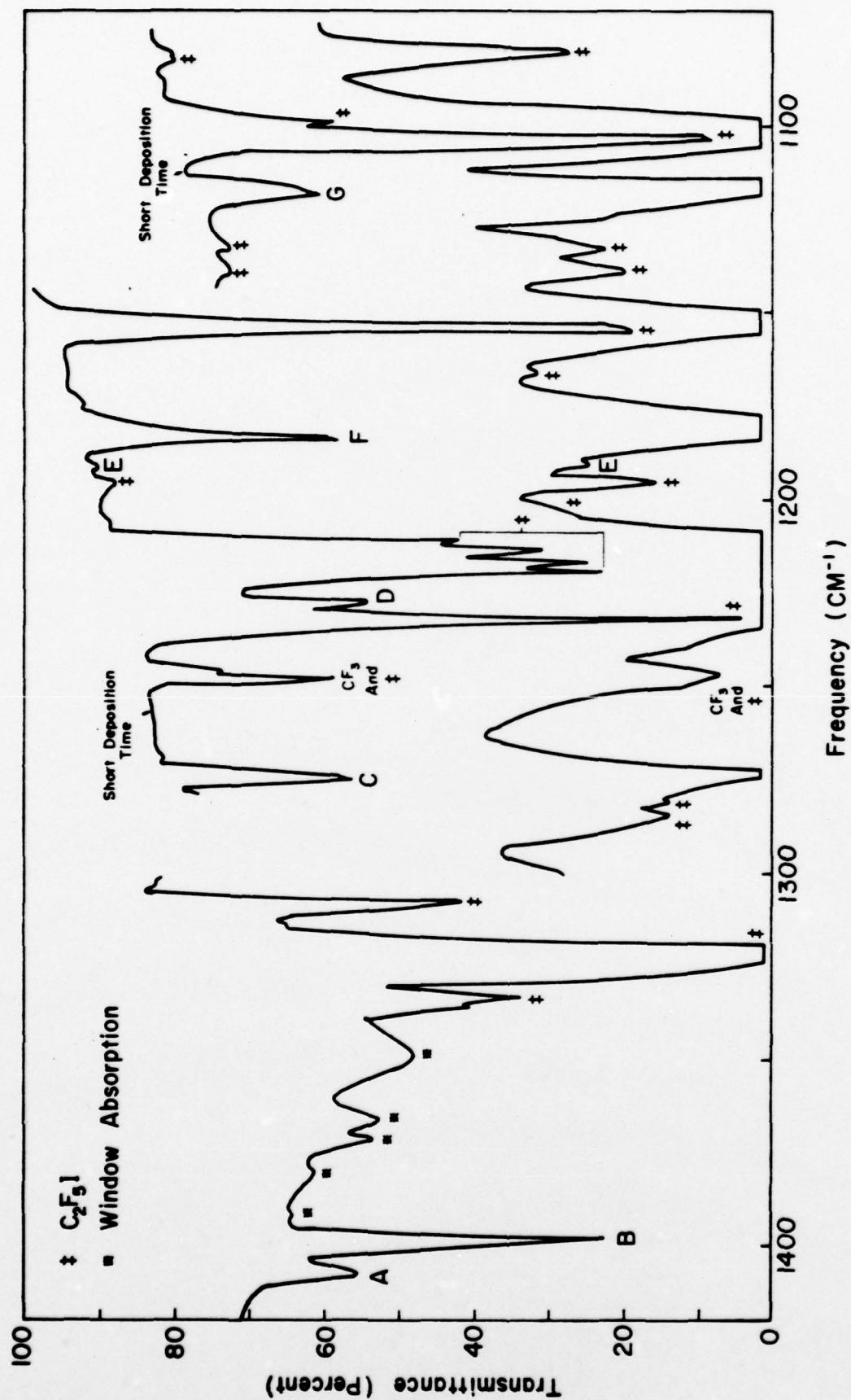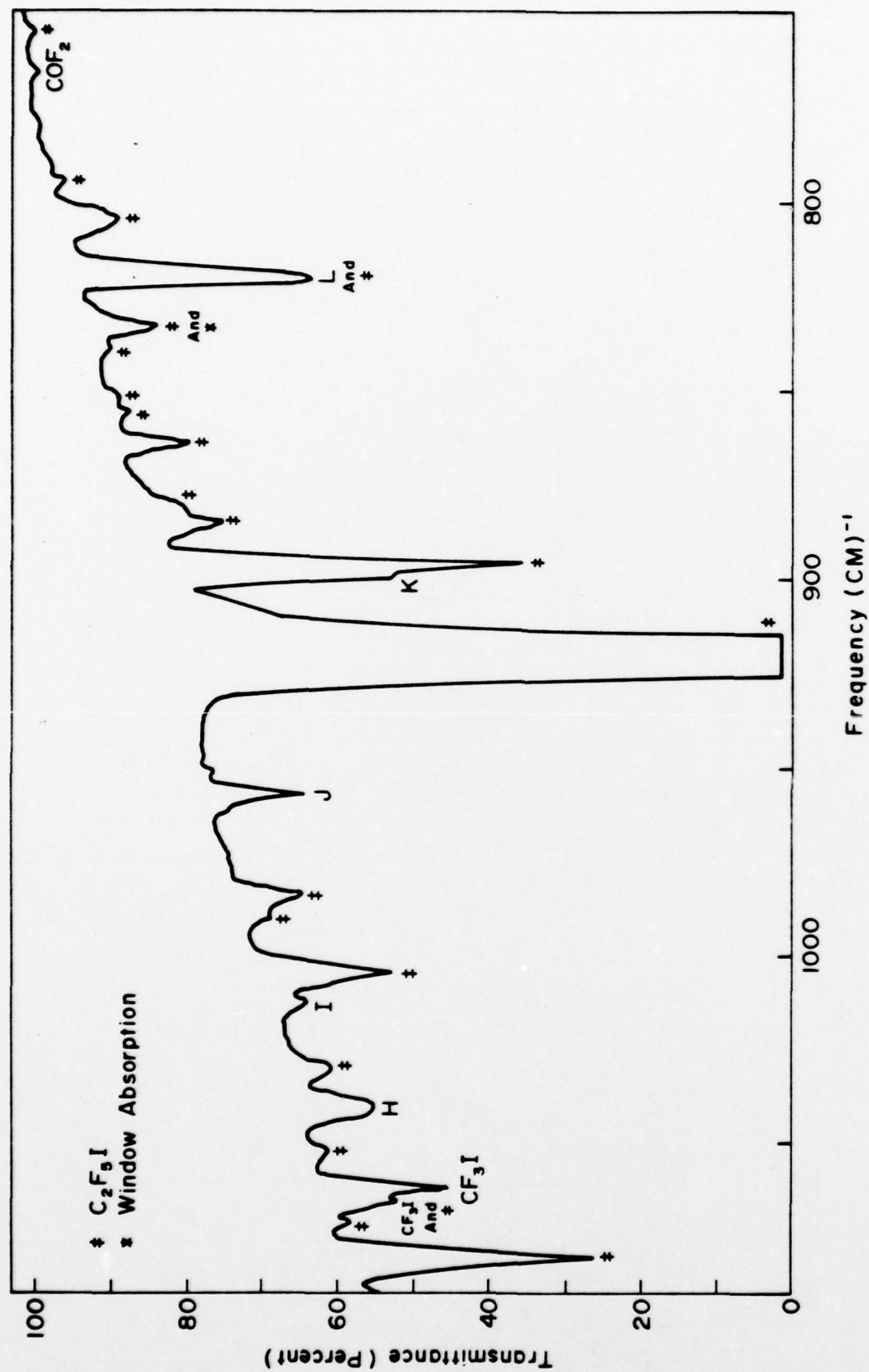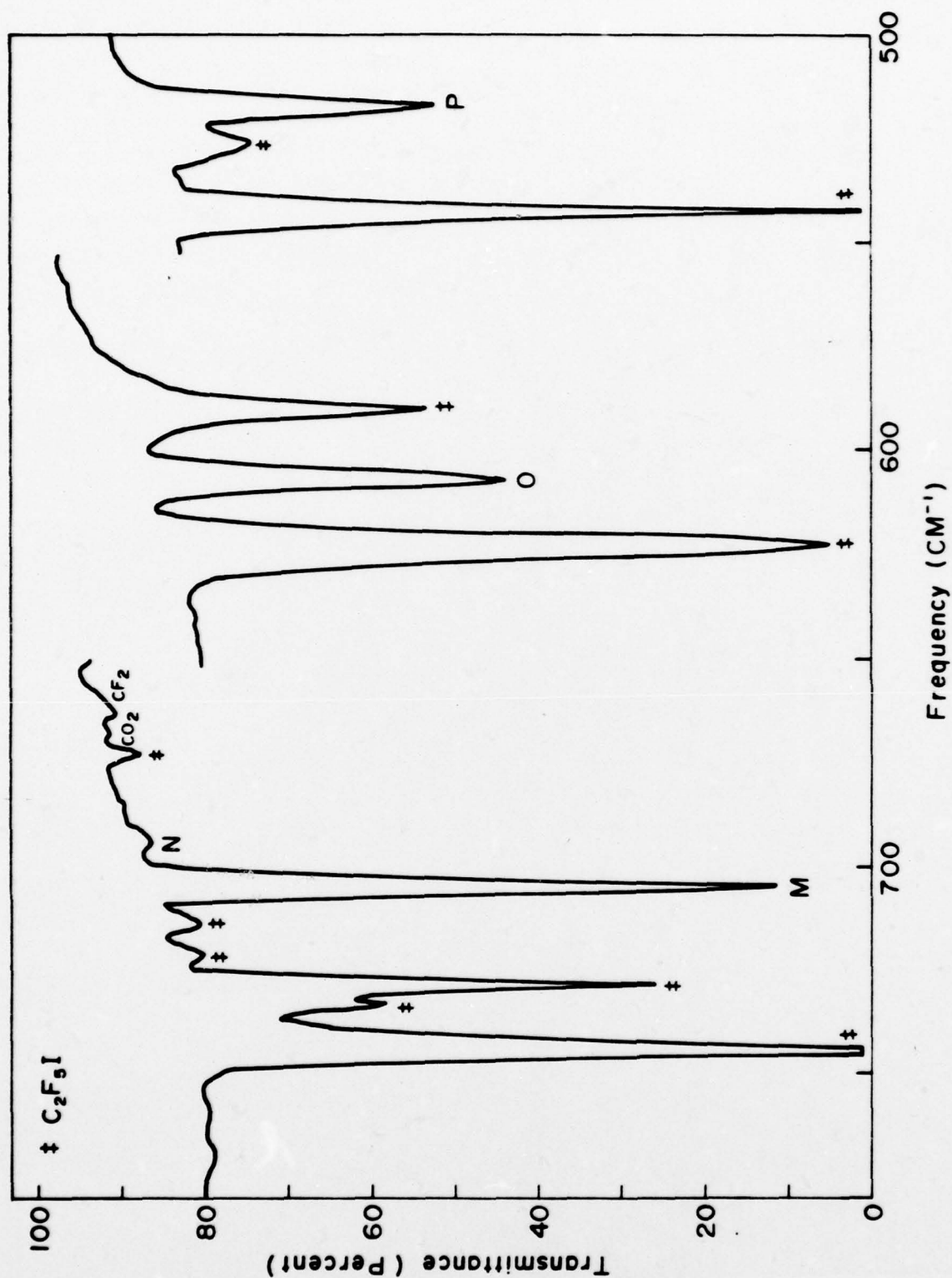
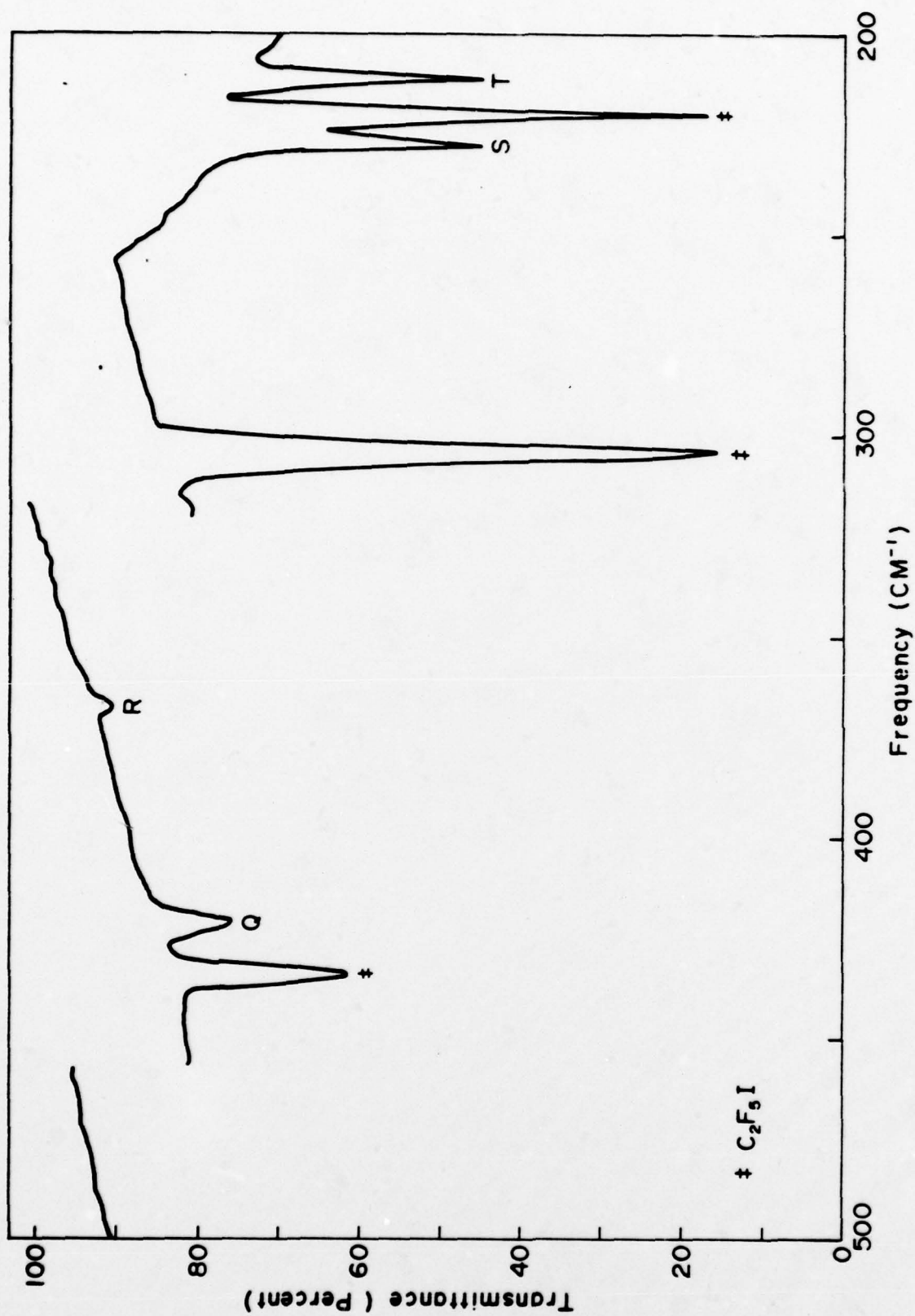Fig. 3 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

Fig. 4   MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF
C₂F₅I (20hr. Deposition)

‡ C₂F₅I

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Table 1

INTENSITY MEASUREMENTS (ABSORBANCE UNITS) OF POSSIBLE C_2F_6 ABSORPTION BANDS

Band	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
Frequency (cm⁻¹)	1410	1398	1273	1227	1193	1184	1117	1040	1012	956	898	820	703	694	604	514	419	366	227	211
Expt.																				
1a	-	-	0.218	0.182	-	0.290	0.153	-	-	-	-	-	0.0185	-	-	-	-	-	-	-
1b	-	-	0.714	0.588	-	0.871	0.416	-	-	-	-	-	0.0783	-	0.0249	-	-	-	-	-
1c	-	-	-	-	-	-	-	-	-	-	-	-	0.392	-	0.124	-	-	-	-	-
2a	-	-	0.460	0.415	-	0.562	0.283	-	-	-	-	-	0.0480	-	-	-	-	-	-	-
2b	-	-	-	-	-	-	-	-	-	-	-	-	0.295	-	0.106	-	-	-	-	-
3	-	-	0.385	0.354	-	0.476	0.221	-	-	-	-	-	0.0411	-	0.0140	-	-	-	-	-
4a	-	-	0.225	0.240	-	0.287	0.146	-	-	-	-	-	0.0191	-	-	-	-	-	-	-
4b	-	-	0.433	0.410	-	0.577	0.262	-	-	-	-	-	0.0484	-	0.0143	-	-	-	-	-
5	-	-	0.162	0.097	-	0.207	0.107	-	-	weak	-	-	0.0150	-	weak	-	-	-	-	-
6	-	-	-	-	0.031	-	-	0.020	-	weak	-	-	0.208	-	0.063	0.047	0.011	-	0.035	0.039
7	-	0.056	-	-	0.017	-	-	0.014	-	-	-	-	0.151	-	0.047	0.033	-	-	0.021	0.025
8	0.015	0.129	-	-	0.030	-	-	0.019	*	0.008	*	*	0.201	0.006	0.061	0.042	0.008	-	0.033	0.040
9a	0.059	0.256	-	-	0.046	-	-	0.039	*	0.020	*	*	0.395	0.010	0.139	0.086	0.019	0.008	0.089	0.082
9b	0.052	0.253	-	-	0.046	-	-	0.047	*	0.036	*	*	0.568	weak	0.197	0.141	0.027	0.011	0.141	0.132
10a	0.024	0.227	-	-	0.020	-	-	0.019	*	0.021	*	*	0.287	-	0.098	0.063	0.011	weak	0.054	0.066
10b	0.054	0.357	-	-	0.047	-	-	0.044	*	0.051	*	*	0.572	0.010	0.195	0.142	0.024	0.010	0.139	0.144
10c	0.076	0.485	-	-	0.049	-	-	0.072	*	0.077	*	*	0.931	0.009	0.308	0.233	0.053	0.015	0.247	0.225

*Too badly overlapped with C_2F_5I band to make intensity measurement.

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compromised. Because of this difficulty, the weaker 604 cm^{-1} absorption band was also used as a reference since it did not suffer interference from any known species.

The standard deviation of the derived relative intensity ratios is presented in Table 2 together with some comments as to experimental difficulties associated with the individual measurements. Not mentioned in this connection are the difficulties associated with spectrometer response. In experiments with heavy matrix deposits, matrix transparency was markedly reduced in the higher (>1,000 cm^{-1}) frequency region. For the weaker bands in this range, optical density measurements are likely to have considerable error. In the low frequency range below 250 cm^{-1}, although matrix transparency was never really bad, the intrinsic spectrometric performance was not very good, due to a combination of low energy and background water vapor absorption.

Because of the above difficulties related to the optical density measurements, it was considered unrealistic to select a single criterion for all the absorption features (i.e., some arbitrary upper limit to the precision of the relative intensity measurements) for determining which absorption bands could have common precursors. Rather, each intensity correlation measurement and its associated standard deviation was considered to see if it fell within a range commensurate with the measurement problems, if indeed the two bands did have a common source. Assuming good instrument response and no problem with defining the correct base line, individual relative intensity measurements can be expected to be accurate to within about 2-12% in the 5-95% transmission range. For bands designated as vvw (Table 2) or those for which peak definition is complicated by partial overlap with other species, making correct base line definition uncertain, the higher limit to the expected accuracy is probably about 45%.

With the above considerations, the intensity correlation data shown in Table 2 may reasonably be taken to indicate that all absorption bands listed could have a common precursor. Assuming the correctness of the conclusion, a better correlation obtains for the data based on the 604 cm^{-1} band (average standard deviation $\bar{\sigma} = \pm15.7\%$) than that obtained from the 703 cm^{-1} band ($\bar{\sigma} = \pm19.1\%$). This is consistent with expectations mentioned earlier due to partial overlap of the 703 cm^{-1} band.

At this point, it will be assumed that the most likely candidate responsible for the absorption bands listed in Table 2 is the radical C_2F_5 and an attempt will be made to assign the observed frequencies on this basis.

Table 2

Relative Intensity Ratios For The 24 "Unknown" Absorption Bands In The Spectrum
of The Pyrolysis Products Of C_2F_5I

Band	Frequency (cm^{-1})	Intensity Correlation With Band at 703 cm^{-1}	Intensity Correlation With Band at 604 cm^{-1}	Remarks
A	1410 (vw)	$\pm$ 21.2%	$\pm$ 24.6%	partially overlapped with band at 1398 cm^{-1}
B	1398 (w)	$\pm$ 27.1%	$\pm$ 18.4%	some interference from window absorption
C	1273 (vs)	$\pm$ 11.7%	$\pm$ 4.8%	
D	1227 (s)	$\pm$ 20.0%	$\pm$ 10.0%	partially overlapped with a C_2F_5I band
E	1193 (vvw)	$\pm$ 38.2%	$\pm$ 40.6%	some overlap with a strong C_2F_5I band
F	1184 (vs)	$\pm$ 13.2%	$\pm$ 9.4%	
G	1117 (s)	$\pm$ 17.9%	$\pm$ 7.6%	
H	1040 (vw)	$\pm$ 14.6%	$\pm$ 17.2%	
I	1012 (vvw)	?	?	partially overlapped with a C_2F_5I band
J	956 (vw)	$\pm$ 32.6%	$\pm$ 27.5%	
K	898 (vw?)	?	?	overlapped with a C_2F_5I band
L	820 (vw?)	?	?	overlapped with a C_2F_5I band
M	703 (m)	reference	$\pm$ 6.4%	reference band for intensity correlations
N	694 (vvw)	$\pm$ 31.2%	$\pm$ 23.9%	
O	604 (w)	$\pm$ 6.4%	reference	reference band for intensity correlations
P	514 (w)	$\pm$ 7.0%	$\pm$ 6.9%	
Q	419 (vw)	$\pm$ 14.6%	$\pm$ 16.9%	
R	366 (vvw)	$\pm$ 10.4%	$\pm$ 7.9%	some interference from a C_2F_5I band
S	227 (vw)	$\pm$ 23.9%	$\pm$ 18.9%	partially overlapped with a C_2F_5I band
T	211 (vw)	$\pm$ 14.9%	$\pm$ 10.7%	

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Very little is known of the structure of C_2F_5. An EPR experiment covering a broad temperature range led to the conclusion that the radical site was pyramidal [14], as in trifluormethyl, and that there was a barrier to rotation about the C—C bond of 11.9 kJ mol^{-1}. Such a structure implies the radical belongs to the C_S point group in which all 15 fundamental frequencies are IR active.

In making the tentative assignment shown in Table 3, earlier frequency assignments made for C_2F_5X (X = H [9], F [8], Cl [8], Br [8], and I [8]), CF_3COX (X = F [10], Cl [11], and OH [12]), and CF_3NF_2 [13] have been used for comparison. Five C—F fundamental stretching modes are expected in the 1400-1100 cm^{-1} region with good intensity. There are five obvious candidates at 1398, 1273, 1184, and 1117 cm^{-1}. The three higher and the two lower sets of frequencies are assigned to CF_3 and CF_2 stretching modes, respectively [8]. The distribution of the frequencies to the specific vibrational modes of the CF_3 group are somewhat questionable. There are some indications that the symmetric CF_3 stretching mode lies at higher frequency than the unsymmetrical mode in many compounds [10,11,12,13] and on this basis the frequency at 1398 cm^{-1} was so assigned. In C_2F_5X (X = Cl, Br, and H), the highest frequency has been assigned to an a'' rather than an a' mode as in the present case.

The two lowest frequencies in Table 3--at 211 and 227 cm^{-1}--are assigned to the ν_9 (a') and ν_{14} (a'') CF_3 rocking modes. By analogy with other molecules, this assignment seems fairly certain. The value of the torsional mode at 67 cm^{-1} was calculated based on the barrier height to internal rotation obtained in the EPR study [14].

The assignment for the specific CF_3 and CF_2 deformation modes is at best somewhat arbitrary. The unsymmetrical modes appear in the 770-540 cm^{-1} region, while the symmetrical modes lie at somewhat lower average frequencies of 660-310 cm^{-1}. There are obviously several frequencies in Table 2 which could be assigned to the CF_3 and CF_2 deformation modes. A total of seven lie in the expected range for these modes of 770-310 cm^{-1}. Because of this situation, the best that can be said of the assignment in Table 3 for the lower bending frequency modes is that qualitatively they are reasonable, but that several other permutations of the frequencies would be just as acceptable.

A similar situation exists for the assignment of the ν_4, C—C stretching frequency. In other carbon-fluorine compounds, the frequency appears to fall within the range 940-750 cm^{-1}. In Table 2, there are three frequencies at 820, 898, and 956 cm^{-1} which could be considered. In addition, there are two

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Table 3

TENTATIVE FUNDAMENTAL FREQUENCY ASSIGNMENT FOR C_2F_5

Vibrational Mode	Frequency cm^{-1}	Approximate Mode Description
Species a'		
ν_1	1398	Sym CF_3 stretch
ν_2	1273	Unsym CF_3 stretch
ν_3	1117	Sym CF_2 stretch
ν_4	820 - 1040?	C—C stretch
ν_5	703	Unsym CF_3 deformation
ν_6	604	Syn CF_3 deformation
ν_7	514	CF_2 deformation
ν_8	419	Sym FCC angle bend
ν_9	227	CF_3 rock
Species a''		
ν_{10}	1227	Unsym CF_3 stretch
ν_{11}	1182	Unsym CF_2 stretch
ν_{12}	694	Unsym CF_3 deformation
ν_{13}	366	Unsym FCC angle bend
ν_{14}	211	CF_3 rock
ν_{15}	67	Torsion

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bands at 1012 and 1040 cm^{-1} which, although at somewhat higher frequencies than noted above, might also be candidates. Although by no means compelling evidence in its favor, it is interesting to note that of the above five frequencies, only that at 1040 cm^{-1} cannot be accounted for in terms of sum or difference frequencies of the other assigned fundamentals. Because of these uncertainties, the assigned C—C stretching mode in Table 3 is simply denoted as the extreme limits covered by the five possible observed frequencies.

There are only two other frequencies in Table 2, at 1410 and 1193 cm^{-1}, which have not been discussed. The former can be interpreted in terms of combination modes of the assigned fundamental, but not the latter. Since this feature is extremely weak and in close proximity to the very strong 1182 cm^{-1} band, it is possible that it may represent some matrix effect on this frequency.

The above may only be regarded as a tentative vibrational assignment for C_2F_5. However, the magnitudes of the frequencies are in a range which would be expected of the radical, assuming that the approximate tetrahedral structure at the radical center is retained. Indeed, the frequencies assigned in this investigation to the C_2F_5 radical are almost identical with those estimated by approximating procedures using C_2F_5H as a model compound and eliminating the three carbon-hydrogen vibration frequencies [14,15]. This finding is reassuring since the latter approximating procedures for carbon-fluorine radicals has only been tested to date on CF_3, for which it also works well, and gives added confidence to this method for estimating frequencies that are required in the computation of thermochemical quantities C_p° and S°. In the near future, we will present a normal coordinate analysis for the C_2F_5 radical based on these results.

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IR MATRIX ISOLATION SPECTRA OF SOME PERFLUORO ORGANIC FREE RADICALS
PART 2, CF_3O_2

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ABSTRACT

The radical CF_3O_2 has been formed by allowing CF_3 radicals, produced by the pyrolysis of CF_3I, to interact during condensation with an oxygen doped argon matrix gas at 12°K. $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$ isotope studies clearly demonstrated the presence of two symmetrically non-equivalent oxygen atoms in the molecule. Assuming C_S symmetry, 10 of the 12 possible fundamental vibrational modes were identified in the spectral range 2000-200 cm^{-1} and a tentative frequency assignment made.

INTRODUCTION

Peroxy radicals of the $CF_nCl_{3-n}O_2$ (n= 0 to 3) are of interest for their possible role in stratospheric photochemistry[1] of halocarbons, and the perfluoro compound, for its possible involvement in combustion inhibition when CF_3Br is used as a fire retardant. Photolysis of CF_3OOF and CF_3OOOCF_3 in argon matrices resulted in the appearance of two absorption bands at 1173 and 1094 cm^{-1} which were tentatively assigned to CF_3O_2.[3] An earlier attempt to form the radical by pyrolysis of CF_3OOCF_3 with subsequent matrix isolation of the products was unsuccessful[4] though indication of formation of some relatively unstable unknown species was obtained. To our knowledge this is the extent of current IR characterization studies on these peroxy-radicals.

Recently in this laboratory we have shown that the pyrolysis approach to producing free radical species for subsequent trapping in inert gas matrices can be used effectively and have demonstrated the method to obtain the IR spectrum of C_2F_5 radical.[5] In this paper we report the infrared spectrum of CF_3O_2 obtained by pyrolysing CF_3I in a low pressure effusion tube and trapping the resultant CF_3 radicals in matrices of oxygen doped argon and pure oxygen.

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EXPERIMENTAL

The basic experimental arrangement has been described previously[5] and only those details peculiar to the present investigation will be noted. In this study, the platinum pyrolysis tube, of the same dimensions as used in the earlier study, was heated resistively rather than inductively. This change was made only because most experiments required pyrolysis temperatures in the 550-650°C range. Such temperatures could be more conveniently measured using a chromel-alumel thermocouple than by using an optical pryometer which is required when using RF heating. Mixtures of CF_3I in argon were prepared containing 0.3-0.05% of the iodide. These gas mixtures, or pure CF_3I (in a few experiments CF_3Br replaced CF_3I) were passed through the pyrolysis tube to produce CF_3 radicals. Oxygen doped argon matrix gases containing from 5-20% O_2 were used; in most experiments the 20% O_2 figure applied. In some experiments isotopically scrambled oxygen, $^{16}O^{18}O$, was used. It was prepared by subjecting equimolar amounts of the pure components in a quartz flask at low pressure to an electric discharge overnight followed by photolysis with Hg arc 2537 $\overset{o}{A}$ radiation to destroy any ozone. Deposition times varied from 30 min. to 15½ hr, with as little as 150 cc to as much as 3300 cc NTP of matrix gas being used. Spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Reported frequencies are accurate to 1.5 cm^{-1} in the 2000-200 cm^{-1} region.

MATERIALS

Linde Ultra High Purity Grade argon and Matheson Research Grade oxygen were used for matrix gases. The following halocarbons; CF_4, C_2F_4, C_2F_6, COF_2, CF_3OF, CF_3OOCF_3, CF_3I and CF_3Br were obtained either from Matheson or Penisular Research Chemicals, Inc. Stated purities ranged from 97 to 99.7%. All these materials were subjected to trap to trap distillation at liquid nitrogen temperatures prior to use. $^{18}O_2$, 99% isotopic purity was obtained from Prochem Isotopes.

RESULTS AND DISCUSSION

In this study it was hoped that CF_3O_2 could be formed by reacting CF_3 radicals with oxygen during the matrix trapping process. Accordingly, CF_3 radicals were produced by pyrolysing CF_3I alone and directing the radicals

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into a matrix gas containing O_2. Indeed a new compound was formed in this way but concomitantly relatively large amounts of CF_4 and COF_2 also resulted. Experiments were tried with argon-oxygen mixtures containing from 5-20% of the latter in an effort to minimize the COF_2 and CF_4 formation with respect to the amount of new compound formed. The only obvious effect this had was to increase the amount of unreacted CF_3 radicals trapped in the matrix at the lower, compared to the higher, O_2 concentrations. Further efforts at reducing COF_2 and CF_4 formation centered on making $Ar + CF_3I$ mixtures and passing these through the pyrolysis tube and directing the total effusate into an oxygen doped argon matrix gas. This approach proved quite success-ful at reducing COF_2 and CF_4 formation relative to that of the new compound. In most subsequent experiments, therefore, about equal volumes of gases were passed through the pyrolysis tube as were separately injected for matrix formation.

As in the earlier study on the C_2F_5 radical, the same general experi-mental approach was followed; first, obtain matrix spectra of CF_3I, its possible stable pyrolysis products and pyrolysis oxidation products (the fluorocarbons listed above); second, obtain matrix spectra of CF_3I pyroly-sis products with and without oxygen in the matrix gas; third, identify known stable and unstable halocarbons (CF_3,[6,7], CF_2,[6,7], and C_2F_5[5]) and oxygenated products (COF_2, COF,[8] FO_2,[9] and FO[10]), and four, use relative intensity measurements on the remaining unassigned absorption bands to identify features associated with common precursors. In addition to the species listed above which might have been formed under the experimental con-ditions used, several others were also considered. Some of these compounds although well characterized were not readily available. Thus, for CF_3OCF,[3] $CF_2(OF)_2$,[11] CF_3OOF,[3] and CF_3OOOCF_3[3] literature IR spectra were used for comparison purposes. The possibility that IO_x compounds might have been formed due to I atom interaction in the matrix was eliminated by deliberately dissociating molecular iodide vapor in the pyrolysis tube and allowing inter-action with an oxygen containing matrix; no absorption bonds attributable to IO_x compounds resulted. The possible formation of IF_x compounds was elimin-ated by comparison with recently obtained matrix spectra[12] of IF, IF_3, I_2F_2, IF_5, and I_2F. Finally, the possible presence of IO_2F and IOF_3 was negated by comparison with literature spectra of these compounds.[13]

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At the pyrolysis temperatures used in the investigation, with pure argon as the matrix gas, it was estimated that $\geq 85\%$ of the iodide was decomposed. CF_3 was the major species formed together with smaller amounts of $CF_2 > CF_4 > C_2F_6$. Increasing the pyrolysis temperature resulted in more CF_2 being produced relative to CF_3. The pyrolysis temperature range chosen was a compromise, aimed at maximizing CF_3I decomposition, and minimizing CF_2 production. From the initial experiments at short deposition times in which CF_3 was isolated in oxygen doped matrices, a cursory examination of the spectra in the 1050-1400 cm^{-1} range clearly showed the almost complete disappearance of the CF_3; the presence of CF_4 and COF_2 at moderate levels; minor amounts of CF_2, C_2F_6 and unreacted CF_3I and several new absorption bands with intensities comparable to or greater than those of the CF_4 and COF_2 not readily assignable to any previously characterized species.

A thorough investigation of these new absorption bands was undertaken. Deposition times of from $\frac{1}{2}$ to 2 hr were sufficient to characterize the high intensity stretching modes in the 1000-1400 cm^{-1} region whereas deposition times of up to 15 hrs were required to obtain spectra of the weaker bending modes. Typical spectra resulting from the isolation of pyrolysed CF_3I in Ar + 20% $^{16}O_2$, Ar + 20% $^{18}O_2$ and pure $^{16}O_2$ matrices are presented in Figures 1, 2, 3, and 4. The only marked difference in the spectra recorded using pure $^{16}O_2$ rather than Ar + (5-20)% $^{16}O_2$ as the matrix gases was the complete absence of CF_3 with the former as opposed to a small amount found with the argon/oxygen mixtures. In the longest duration experiments the only other fluorine compound unambiguously identified, not noted above from the initial studies, was FO_2 at very low levels.

In the most intense spectra ($^{16}O_2$ experiments) a total of some 55 absorption bands were identified in the 2000-200 cm^{-1} region which could not be readily assigned to known compounds. Absorption band intensity measurements were made on all these features, though most of them, even in the most intense spectra, were extremely weak. Similar measurements were made on spectra containing the pure $^{18}O_2$ isotope. Absorption band intensity data were only measured from spectra in which Ar + 20% O_2 matrices were used in an effort to minimize possible matrix site effects on absorption bond intensities due

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FIG. I MATRIX ISOLATION SPECTRA OF PYROLYSIS PRODUCTS OF
CF$_3$I IN 20% ^{16}O$_2$ + 80% Ar (top), 20% ^{18}O$_2$ + 80% Ar (middle) &
100% ^{18}O$_2$ (bottom)

FIG. 2 MATRIX ISOLATION SPECTRA OF PYROLYSIS PRODUCTS OF
CF$_3$I IN 20% ^{16}O$_2$+80% Ar (top), 20% ^{18}O$_2$+80% Ar (middle) &
100% ^{18}O$_2$ (bottom)

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FIG. 3 MATRIX ISOLATION SPECTRA OF PYROLYSIS PRODUCTS OF
CF₃I IN 20% ¹⁸O₂ + 80% Ar (top), 20% ¹⁶O₂ + 80% Ar (middle) &
100% ¹⁶O₂ (bottom)

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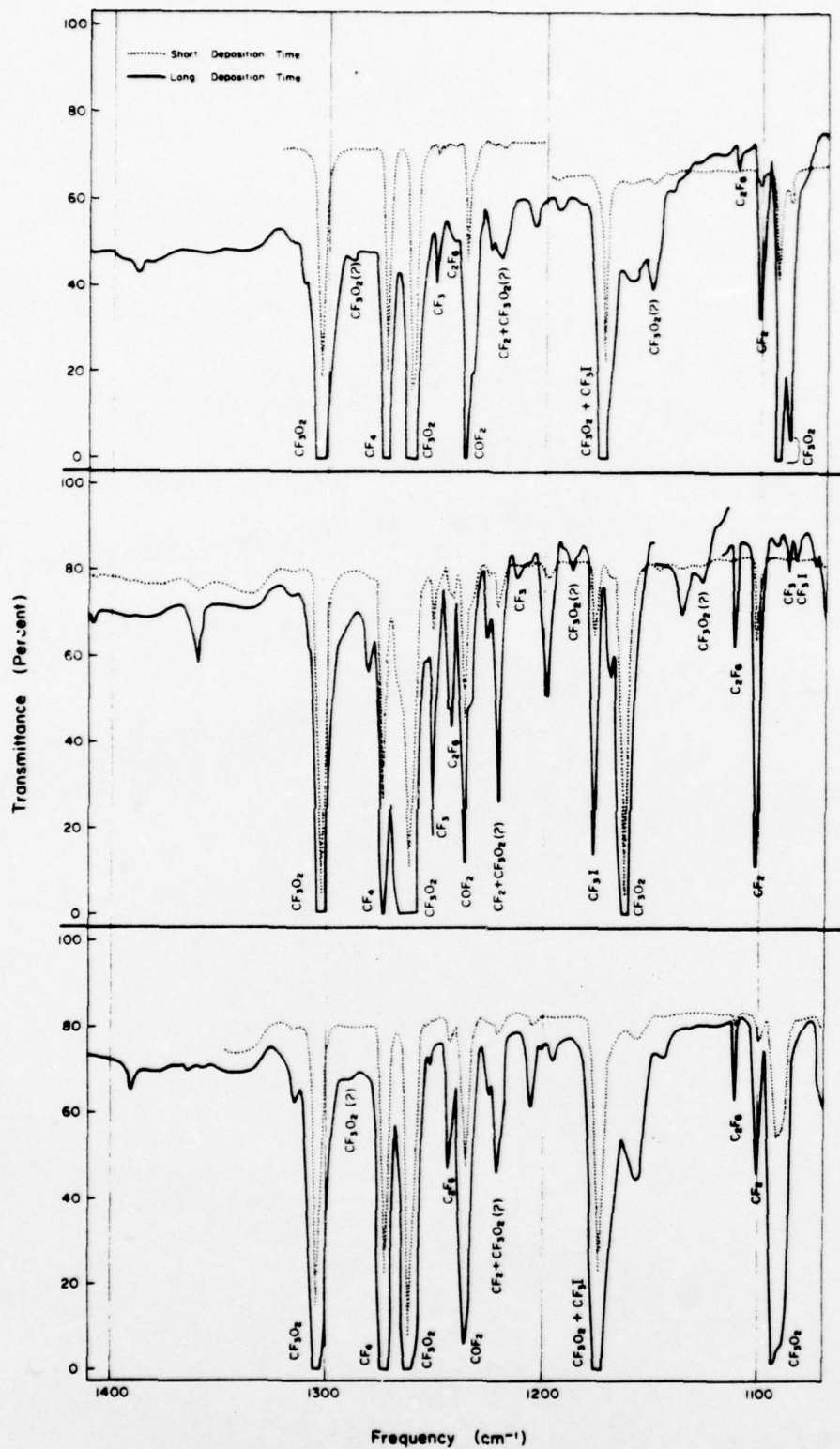
FIG. 4 MATRIX ISOLATION SPECTRA OF PYROLYSIS PRODUCTS OF
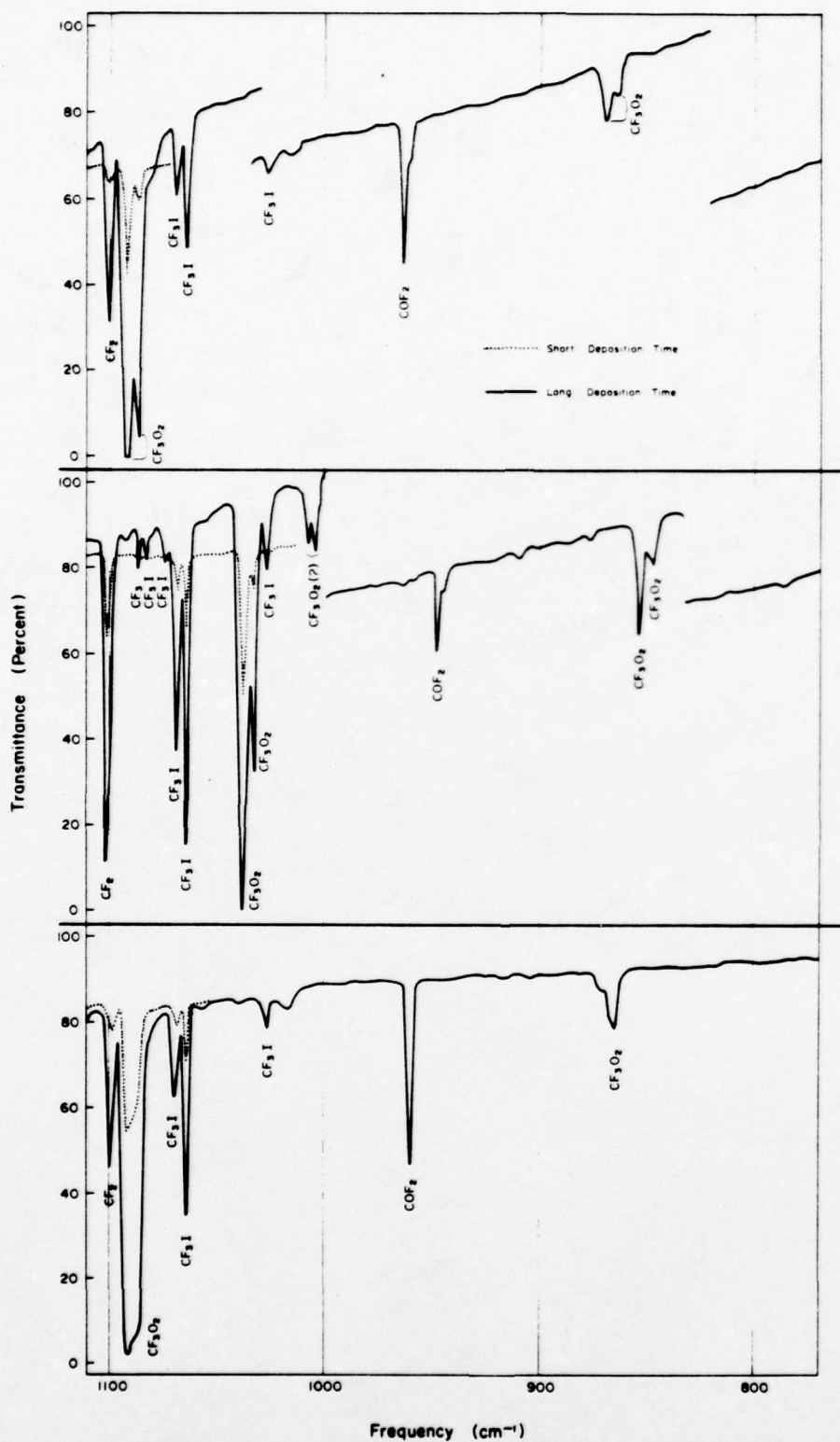CF₃I IN 20% ¹⁸O₂ + 80% Ar (top), 20% ¹⁸O₂ + 80% Ar (middle) &
100% ¹⁸O₂ (bottom)

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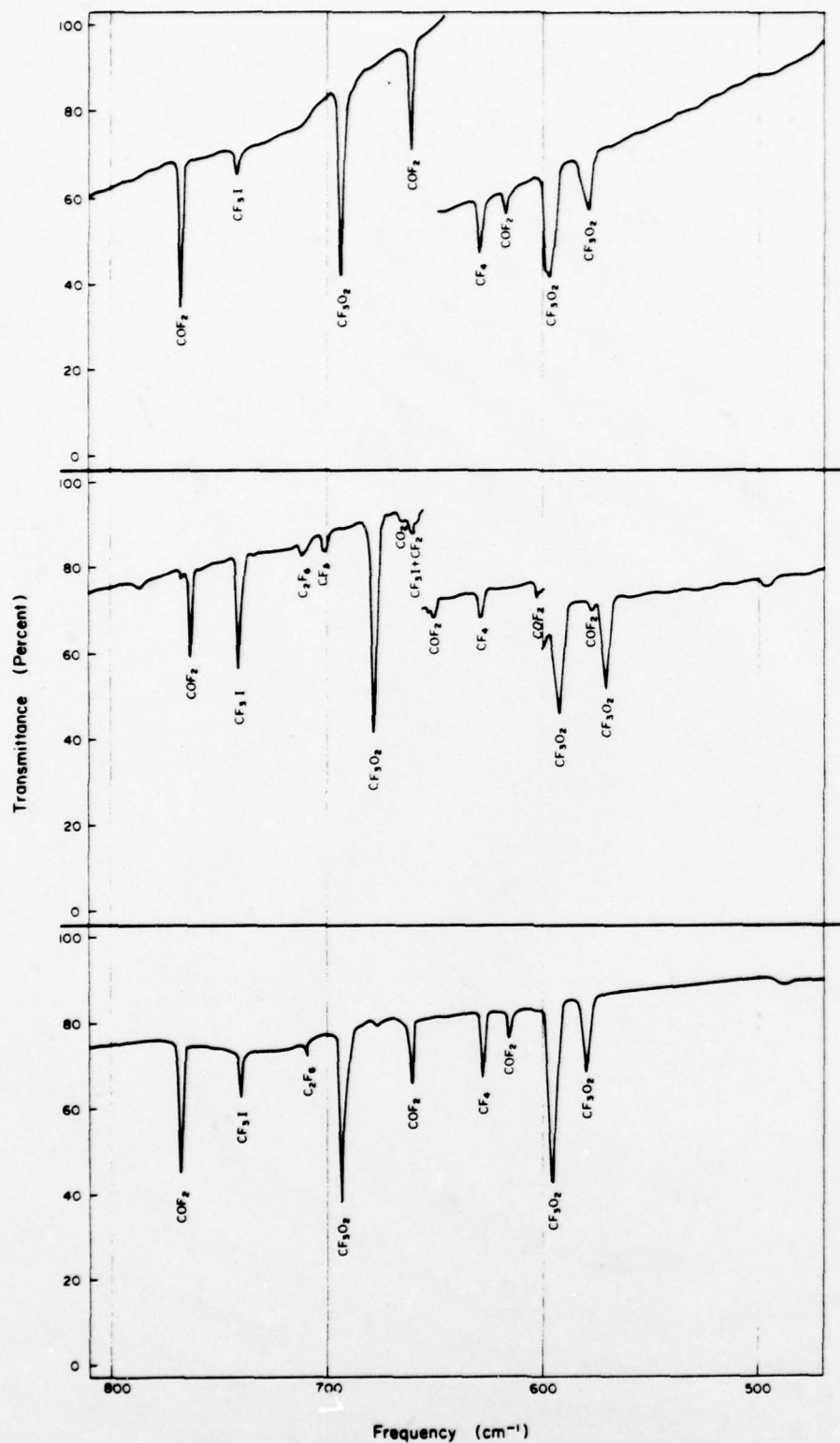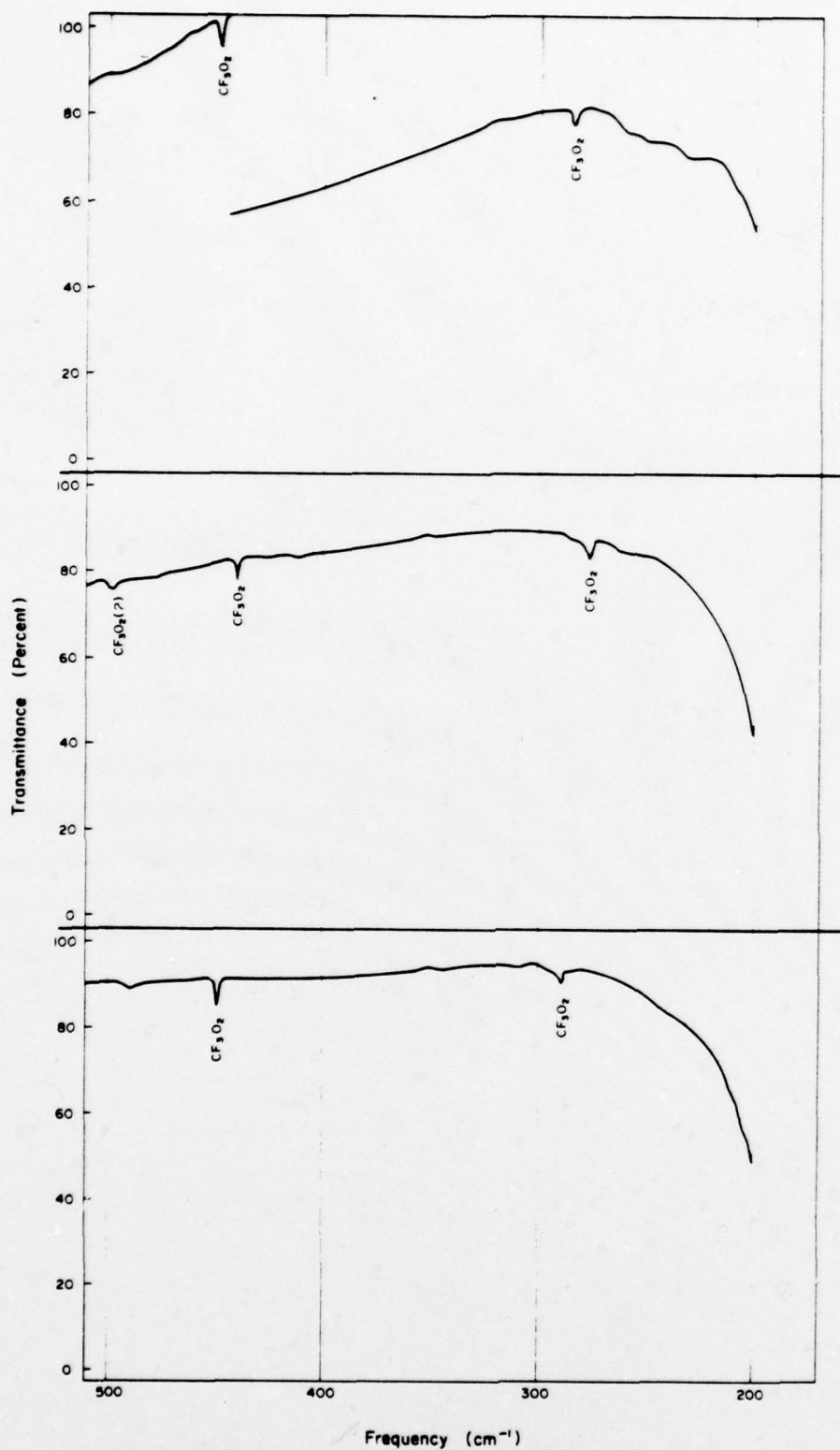to different matrix environments. Based on the observed shifts of <1 cm^{-1} for absorption bonds in spectra recorded in matrices containing 5% and 20% O_2, respectively it appears that matrix effects probably did not have much effect on the measured absorption band intensities. In Tables 1 and 2 absorption band intensity values are presented from measurements on the $^{16}O_2$ and $^{18}O_2$ spectra, respectively. Obviously each of these compilations lists less than the total number of absorption features observed experimentally. However, the absorption bands tabulated in the Tables 1 and 2 had the property that relative intensity measurements indicated they could all be assigned to the same molecular species in their respective matrices. These relative intensity data measurements are presented in Tables 3 and 4. In both cases relative intensities were determined with respect to two absorption bands in each spectra which did not suffer any obvious overlap with other features. As noted in the previous paper,[5] individual relative intensity measurements can be expected to have an error of between $\pm(2-12)$% when the transmission at the measured bands is in the 5-95% region and there are not instrumental response or overlap problems. When the latter is not the case or absorption bands are designated as vvw, the accuracy may be no better than ±45%. Using these criteria, the assignment of all the absorption bands listed in Tables 3 and 4 to a single precursor in each case may be justified.

An attempt will now be made to assign these absorption bands to a specific molecular species. From a consideration of the spectra resulting with $^{16}O_2$ or $^{18}O_2$ in the matrix gas it is apparent that some absorption features show a pronounced and obvious isotope effect, notably doublets at 1092-1086 and 870-864 cm^{-1}, and singlets at 1172, 692, 597, 580, 448, and 286 cm^{-1} in the $^{16}O_2$ containing matrix. The corresponding bands in the $^{18}O_2$ containing matrix, are doublets at 1038-1032, and 854-848 cm^{-1} and singlets at 1162, 678, 594, 572, 440 and 276 cm^{-1}. These findings unequivocally prove the presence of a molecule containing at least one oxygen atom. In experiments in which a mixture of $^{16}O_2$: $^{16}O^{18}O$: $^{18}O_2$ in the ratio 1:2:1 was used as the dopant in the argon matrix gas, three sets of absorption bands clearly appeared as quartets of approximately equal intensity; features at 1172, 1168, 1165, and 1162 cm^{-1}, 1092, 1070, 1064, and 1038 cm^{-1} and 692, 690, 682, and 678 cm^{-1}. Other absorption bands referred to earlier in the pure $^{16}O_2$ and $^{18}O_2$ spectra also

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Table 1

INTENSITY MEASUREMENTS (ABSORBANCE UNITS) OF PROBABLE $CF_3{}^{18}O{}^{16}O$ BANDS

Expt. No.	Frequency (cm⁻¹) 1303	1290	1260	1221	1172	1150	1092	1086	870	864	692	661	597	580	448	286
1	0.339	0	0.398	0	0.276	0	0.119	0.034	0	0	0.012	0	weak	0	0	0
2	0.230	0	0.290	0.008	0.201	0	0.096	0.014	0	0	0.008	0	0.006	0	0	0
3	0.609	0	0.745	0.028	0.497	0.013	0.216	0.038	weak	0	0.023	0.009	0.010	weak	-	-
4	0.665	0	0.707	0.041	0.557	0	0.266	0.048	-	-	-	-	-	-	-	-
5a	1	0	1	0.074	1	0.032	0.759	0.140	0.017	0.007	0.074	0.091	0.045	0.025	0.007	0.008
5b	1	0.023	1	1.193	1	0.432	1	1	0.185	0.075	1	0.740	0.508	0.282	0.084	0.062
5c	-	-	-	-	-	-	-	-	0.569	0.222	1	1	1	0.786	0.177	0.119
7a	0.288	0	0.407	0	0.243	0.007	0.106	0.019	0	0	0.010	0.082	0.024	0	0	0
7b	0.687	0	1	0.010	0.567	weak	0.293	0.109	weak	weak	0.023	0.133	-	weak	0	weak
7c	1	0	1	0.016	1	0.024	0.835	0.218	weak	weak	0.064	0.241	-	weak	weak	weak
8a	0.639	0	0.673	0.052	0.539	0.008	0.229	0.053	weak	0	0.024	0.145	weak	weak	0	0
8b	1	0	1	0.770	1	0.059	1	0.312	0.038	0.013	0.159	0.156	0.081	0.067	0.018	0.012
9a	1	0	1	weak	1	0.027	0.575	0.109	0.014	0.006	0.057	0.011	0.034	0.020	weak	weak
9b	1	-	1	0.262	1	0.152	1	1	0.076	0.038	0.359	0.039	0.178	0.115	0.035	0.023
9c	1	-	1	1	1	0.740	1	1	0.206	0.111	1	0.149	0.555	0.317	0.089	0.063
17a	0.575	0	0.680	weak	0.473	weak	0.203	0.043	weak	weak	0.021	0.033	0.017	small	0	0
17b	1	0	1	0.026	1	0.031	0.592	0.144	0.017	0.011	0.074	0.048	0.048	0.025	0.009	weak
17c	1	0.013	1	0.105	1	0.127	1	1	0.068	0.024	0.312	0.127	0.206	0.089	0.031	0.020

1 - too intense to measure

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Table 2

INTENSITY MEASUREMENTS (ABSORBANCE UNITS) OF PROBABLE CF,^{10}O^{18}O BANDS

Expt. No.	Frequency (cm⁻¹) 1302	1259	1220	1187	1162	1127	1038	1032	1007	1003	878	854	848	788	678	594	572	497	440	276
14a	1.210	0.891	0.066	0	1.144	weak	0.209	0.042	weak	weak	0	0.016	weak	0	0.035	0.016	0.015	0	0	weak
14b	I	1	0.336	0.017	1	0.019	1.039	0.216	0.036	0.039	weak	0.078	0.014	weak	0.184	0.102	0.081	0	0.017	weak
14c	I	1	1	weak	1	0.038	1	1	0.094	0.103	0.014	0.181	0.038	0.012	0.465	0.264	0.199	0.014	0.035	0.035
15a	1.234	0.869	0.056	0	1.235	0	0.226	0.033	0.007	0.008	0	0.017	weak	0	0.036	0.018	0.016	0	0	0
15b	I	1	0.179	0.014	1	0.017	0.687	0.110	0.022	0.030	0	0.052	0.012	0	0.122	0.062	0.049	weak	0.010	0.008
15c	I	1	0.504	0.033	1	0.037	1	0.369	0.070	0.080	0.010	0.146	0.036	0.009	0.338	0.192	0.147	0.011	0.025	0.025
15d	I	1	1	0.067	1	0.070	1	1	0.158	0.181	0.020	0.336	0.092	0.020	1	0.448	0.331	0.020	0.064	0.061

I - Too intense to measure

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Table 3

RELATIVE INTENSITY RATIOS FOR PROBABLE CF_3OO BANDS FROM EXPERIMENTS USING $^{16}O_2$

Frequency (cm⁻¹)	Assignment	Intensity Correlation With Band at 870 cm⁻¹	Intensity Correlation With Band at 692 cm⁻¹	Remarks
1303 (vs)	ν_1	too intense	5 [a]	too intense to correlate with band at 870 cm⁻¹
1290 (vvw)	$\nu_5+\nu_6$	30	too weak	too weak to correlate with band at 692 cm⁻¹
1260 (vs)	ν_2	too intense	7	too intense to correlate with band at 870 cm⁻¹, overlapped with CF_4
1221 (m?)	?	?	?	
1172 (s)	ν_9	too intense	4	severe overlap with CF_2
1150 (w)	$\nu_4+\nu_{11}, \nu_3+\nu_{12}$	28	16	
1092 (m) }	ν_3	12	15	
1086 (m) }		28	38	overlapped with CF_3
870 (w) }	ν_4	reference	6	
864 (vw) }		22	25	
692 (m)	ν_5	6	reference	
597 (w)	ν_6	10	19	partially overlapped with spectro-photometer grating change
580 (w)	ν_{10}	8	12	
448 (vw)	ν_7	14	11	
286 (vw)	ν_{11}	24	26	overlapped with COF_2

[a] Standard deviation of the measurements.

Table 4

RELATIVE INTENSITY RATIOS FOR PROBABLE CF₃OO BANDS FROM EXPERIMENTS USING $^{18}O_2$

Frequency (cm⁻¹)	Assignment	Intensity Correlation With Band at 854 cm⁻¹	Intensity Correlation With Band at 678 cm⁻¹	Remarks
1302 (vs)	ν_1	2	1	
1259 (vs)	ν_2	6	3	overlapped with CF₄, possibly two bands
1220 (m?)	$\nu_9+\nu_{12}, \nu_3+\nu_8$	?	?	severe overlap with CF₂
1887 (vw)	$2\nu_6$	13	11	
1162 (vs)	ν_9	1	3	
1127 (vw)	$\nu_4+\nu_{11}$	19	21	
1038 (s) }	ν_3	1	5	
1032 (m) }		14	13	
1007 (w)	$\nu_{10}+\nu_7$	8	5	
1003 (w)	?	7	7	
878 (vvw)	$\nu_6+\nu_{11}$	12	too weak	too weak to correlate with band at 678 cm⁻¹
854 (w) }	ν_4	reference	8	
848 (vw)		15	15	
788 (vvw)	$\nu_6+\nu_8, \nu_4+\nu_{12}$	4	2	
678 (m)	ν_5	8	reference	
594 (w)	ν_6	13	8	
572 (w)	ν_{10}	6	3	
497 (vvw)	?	13	6	
440 (vw)	ν_7	9	10	
276 (vw)	ν_{11}	9	5	

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showed indications of a quartet structure but overlap with themselves or other absorption bands precluded definite assignment. These data can be reasonable interpreted only in terms of a molecule containing two oxygen atoms unsymmetrically disposed within the molecule.

The the CF_3 radical, known to be present in the effusate leaving the pyrolysis tube, essentially disappeared on interaction with the oxygen containing matrix proves that the new molecular species is a result of an interaction between CF_3 and the oxygen. The presence of a relatively large number of absorption bands assignable to a single precursor indicates a moderate sized molecule, and CF_3O_2 appeared to be the most likely candidate.

From kinetic studies CF_3O_2 has been postulated as an intermediate in the photo-oxidation of CF_3X (X = Cl, Br and I).[14] The compound CF_3NO, is readily formed by the reaction between CF_3 radicals and NO.[12] An activation energy of 0.7 ± 1 kj, was reported[15] suggesting that the reaction between CF_3 and O_2 may also be expected to occur easily. Two experiments were performed in which CF_3 radicals were allowed to interact with NO rather than O_2 doped matrices and indeed the formation of CF_3NO was easily identified from the resulting spectra.[16] That the formation of the new compound was independent of the CF_3 radical source was demonstrated by using CF_3Br as a source of CF_3 radicals to interact with the oxygen doped matrix. The resultant spectra were identical with those obtained from the pyrolysis of CF_3I except for the presence of absorption features attributable to the unreacted bromide.

On the basis of the above it is assumed that the absorption bands listed in Tables 3 and 4 may be assigned reasonably to a species CF_3O_2 containing the $^{16}O_2$ and $^{18}O_2$ isotopes, respectively, A tentative frequency assignment will be presented. The experimental spectral data require the two oxygen atoms to be symmetrically non-equivalent, a geometry which can be attained with the C-O-O skeleton linear or bent. A bent configuration is suggested by analogy with the reasonable well established structures of HO_2[17], DO_2[18] FO_2[15] and CF_3OOCF_3.[18] A linear configuration requiring only 8 fundamental

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IR active frequencies also appears unlikely in view of the larger number observed experimentally. CF_3O_2 with a non-linear configuration belongs to the C_S point group with twelve IR active fundamental virbration frequencies, eight a' and four a'' modes.

In making the tentative frequency assignment shown in Table 5, published data for similar molecules such as CF_3NO,[13] CF_3COF,[20] CF_3OF,[21] and CF_3OOCF_3[19] have been used. Three C-F fundamental stretching frequencies are expected in the 1100-1400 cm^{-1} region with good intensity and there are three obvious condidates at 1303, 1260, and 1172 cm^{-1} [$^{16}O_2$] and comparable frequencies in the [$^{18}O_2$] spectra at 1302, 1259, and 1165 cm^{-1}. The isotopic frequency shift is small for the two higher frequencies as would be expected for modes largely associated with the C-F stretching vibrations. The somewhat larger isotopic frequency shift for the lowest frequency of the triad is consistent with the results of normal coordinate calculations for similar molecules which indicates substancial mixing of the symmetry coordinates for some modes which makes assignments to specific vibrational motions somewhat less meaningful. As with similar molecules the two higher frequencies are assigned to a' modes, and the lower to an a'' mode.

The next highest frequencies at 1092 ($^{16}O_2$) and 1038 ($^{18}O_2$) cm^{-1} can be assigned immediately to the 0-0 stretching mode by virtue of the large observed frequency shift. These frequencies were reported in an earlier study[3] and on the basis of the isotope shift and the magnitude of the frequencies tentatively assigned to CF_3O_2. The C-O stretching mode would be expected to show an isotope frequency shift effect of $\approx 2\%$, and indeed the frequencies at 870 ($^{16}O_2$) and 854 ($^{18}O_2$) cm^{-1} show such a shift and are thus assigned to this mode.

The assignment of the remaining frequencies to C-F deformation modes as shown in Table 5 is entirely reasonable by comparison with similar molecules though other permutations of the frequencies could also be accepted. The $\approx 2\%$ isotope frequency shift associated with ν_5, assigned as a CF_3 deformation, bespeaks of considerable mixing of the symmetry coordinates for this mode. The skeletal bend ν_7 was so assigned because the observed

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Table 5

TENTATIVE FREQUENCY ASSIGNMENT FOR CF_3O_2 OF C_s SYMMETRY

Table I	ν_{1b}	$\nu_{16}\nu_{1u}$		ν_{1u}	Approximate Mode Description
ν_1	1303	--	--	1302	CF_3 stretch
ν_2	1260	--	--	1259	FCF_2 stretch
ν_3	1092	1070	1064	1038	O-O stretch
ν_4	870	868?	852?	854	C-O stretch
ν_5	692	690	682	678	CF_3 deformation
ν_6	597	overlapped		594	FCF_2 deformation
ν_7	448	446?	442?	440	skeletal bend
ν_8	[190]	--	--	--	CF_3 rock
ν_9	1172	1168	1165	1162	FCF_2 stretch
ν_{10}	580	too weak		572	FCF_2 deformation
ν_{11}	286	too weak		276	CF_3 rock
ν_{12}	[120]	--	--	--	torsion

A' brackets ν_1–ν_8; A" brackets ν_9–ν_{12}.

Frequencies in parentheses are estimated.

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isotope shift of $\approx 2\%$ is of the expected order of magnitude, and frequencies in the same range were so assigned in CF_3NO and CF_3OF. The frequency of the CF_3 rocking mode, ν_8, was presumed to lie above the wavelength limit of the present investigation of 50 μ. In similar molecules this frequency has been assigned values either slightly above or below 200 cm^{-1} and a value of 190 cm^{-1} was so estimated. The torsional mode, ν_{12}, was assigned at 120 cm^{-1}, the same value as found in CF_3OF.[22,23]

With the above tentative vibrational assignment for CF_3O_2 it is possible to account for all the absorption bands listed in Tables 3 and 4 which are not fundamentals in terms of combination or difference modes with the exception for a "vvw" band at 497 cm^{-1} in the CF_3 $^{18}O_2$ spectrum. It was noted earlier that in the most intense spectra there were many very weak absorption bands which could not be assigned unequivocally to known stable species, or on the basis of relative intensity measurements, to CF_3O_2. This should not be taken as an indication that they could not possibly originate in the above species, but simply that because the bands were so weak or partially overlapped by other features it seemed prudent not to attempt an assignment. Finally, in the near future a normal coordinate analysis, based on the above data for CF_3O_2, will be presented.

ACKNOWLEDGEMENT

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IR MATRIX ISOLATION SPECTRA OF SOME PERFLUORO ORGANIC FREE RADICALS PART 3, n-C_3F_7 AND iso-C_3F_7

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ABSTRACT

The perfluoro-radicals n-C_3F_7 and iso-C_3F_7 have been prepared by pyrolysing the corresponding iodides in a platinum effusion tube at temperatures in the 450-550°C range and isolated in argon matrices. By elimination of absorption bands attributed to known fluorine compounds and the application of relative absorption band intensity correlations, some 30(n-C_3F_7) and 29(iso-C_3F_7) absorption bands have been assigned to the respective radical species in the spectral range 2000-200 cm^{-1}. A tentative vibrational assignment is presented for both species on the assumption of C_s symmetry. Some thermodynamic implications of the findings are discussed.

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INTRODUCTION

In previous papers in this series the results of studies have been described in which the pyrolyses of perfluoro-organic iodides have been used as radical sources for the characterization via IR matrix isolation spectroscopy of CF_3O_2[1] and C_2F_5[2]. These studies have been further extended, and the pyrolyses of n-C_3F_7I and iso-C_3F_7I used as sources of the corresponding per-fluoro-radicals for matrix IR characterization. To date the only structural data on these radicals have come from EPR studies[3] which show the radical centers to be non-planar. No IR spectral data have been reported.

EXPERIMENTAL

The experimental arrangement used in the study has been described previously, only those details pertinent to the present study will be noted. The two perfluoro-propyl iodides were obtained from PCR Research Chemicals Inc., purities were not stated. Prior to use both materials were purified by trap-to-trap distillation in the vacuum line. The IR spectra of the individual compounds indicated isomeric purity, though a small amount of C_2F_5I, < 1% was present in the n-C_3F_7I. Pyrolysis temperatures of 530-455°C and 550-475°C were used for the n- and iso compounds, respectively. Matrix deposition times varied from 1.5 to 45 hrs. The iodides were leaked into the pyrolysis tube at rates of 8×10^{-7} to 5×10^{-5} mole hr^{-1}. Argon matrix gas flow rates varied from 50 to 150 cm^3 NTP hr^{-1}. The following perfluorocarbons were obtained from PCR Research Corp. Inc., or from Matheson, CF_4, C_2F_4, C_2F_6, C_3F_6, cyclo-C_3F_6, C_3F_8, and n-C_6F_{14}. Stated purities ranged from 97 to 99.7% all were subjected to vacuum line purification procedures prior to use. Spectra were recorded on a Perkin Elmer IR spectrophotometer, Model 283. Reported frequencies are accurate to 1.5 cm^{-1} in the 2000-200 cm^{-1} region.

RESULTS

The general experimental approach used in the study was one; to obtain matrix spectra of n-C_3F_7I, iso-C_3F_7I and their possible stable pyrolysis products (the fluorocarbons listed above); two; to obtain matrix spectra of the products from pyrolyses of C_3F_7I; three; to identify known stable and, unstable (CF_2, CF_3, and C_2F_5) halocarbons in the resulting spectra;

and four; to make relative intensity measurements on the remaining unknown absorption bands to identify common precursor species.

Preliminary experiments were tried with each iodide to determine the best temperature ranges for pyrolysis. The chosen temperatures were a compromise between maximising carbon-iodine bond fission and minimizing subsequent further radical decomposition. Iodide decomposition varied between about 30-60%. In addition to the obvious production of a new species in the n-and iso-C_3F_7I systems, there were fairly substaintial amounts of C_2F_4, CF_3, and CF_2 in the n-C_3F_7I pyrolyses, and C_3F_6, C_2F_4, CF_3, and CF_2 in the iso-C_3F_7I pyrolyses. C_3F_6 and C_3F_8 were very minor products in the former and latter systems, respectively. In both systems lower temperatures minimized these "unwanted" products with respect to the overall pyrolysis.

Spectral data from twelve and eleven pyrolysis experiments were recorded for n-C_3F_7I and iso-C_3F_7I, respectively. Typical spectra are shown in Figures 1 through 6. It was apparent from the spectra that absorption band overlapping of the parent iodide and its decomposition products occurred frequently. This behavior added considerably to the difficulty in making absorption band intensity measurements, being particularly severe in the n-C_3F_7I pyrolysis spectra. Despite these difficulties absorption band intensity measurements were attempted, though in the pyrolysed n-C_3F_7I spectra the overlap problem was too severe with many of the absorption bands for a meaningful measurement to be made. The absorption band intensity measurements for the unknown absorption features obtained in the pyrolysis of n-C_3F_7I and iso-C_3F_7I are presented in Tables 1 and 2. The relative absorption band intensity ratios based on these measurements are shown in Tables 3 and 4.

DISCUSSION

Details of the mechanism of the low pressure pyrolysis of n-C_3F_7I and iso-C_3F_7I are not available. A recent determination[4] showed the C-I bond energy to be the same in both compounds at 49.2 kcal mol^{-1}, only slightly less than in CF_3I (52.6 kcal mol^{-1}) and C_2F_5I (50.6 kcal mol^{-1}). By analogy with the pyrolysis behavior of the latter two compounds[1,2] simple C-I bond fission would appear to be the predominant primary process in the C_3F_7I

Table 1

Intensity Measurements (Absorbance Units) of Probable n-C₃F₇ Bands

Band	b	c	k	l	n	o	s	u	v	w	x	y	z	aa	bb	cc	dd
Expt. Frequency (cm⁻¹)	1287	1285	1116	1114	1016	958	638	608	572	549	520	472	465	401	395	306	273
35	0.510	0.552	0.139	0.176	0.254	0.008	0.034	0.014	weak	0.010	0.014	0	0	0	0	0	0
36	0.371	0.339	0.105	0.128	0.182	weak	0.0251	0.0070	0.0034	0.0064	0.0065	0	0	0	0	0	0
37	0.405	0.437	0.109	0.136	0.200	weak	0.0272	0.0108	0.0049	0.0097	0.0108	0	0	0	0	0	0
38	0.385	0.417	0.099	0.123	0.189	0.008	0.024	0.009	weak	weak	0.011	0	0	0	0	0	0
39	0.566	0.617	weak	0.135	0.262	0.009	0.034	0.009	0.006	0.011	0.013	0	0	0	0	0.012	0.024
40	0.098	0.112	0.025	0.029	0.044	0	weak	weak	0	0	0	0	0	0	0	0	0
41	0.179	0.190	0.050	0.056	0.076	0	weak	weak	0	0	weak	0	0	0	0	0	0
42	0.279	0.311	0.078	0.090	0.136	0	weak	weak	weak	weak	0.009	0	0	0	0	0	0
43	0.205	0.222	-	weak	0.091	0	weak	0.005	weak	weak	weak	0	0	0	0	0	0
44	0.964	I	-	weak	0.394	0.008	0.051	0.017	0.008	0.012	0.016	0.0091	0.0117	0	0	0	0.035
45	I	I	-	weak	I	0.023	0.156	0.053	0.025	0.040	0.042	0.031	0.037	0.005	0.008	0.046	0.084
46	I	I	-	-	I	0.055	0.408	0.121	0.056	0.097	0.106	0.062	0.072	0.010	0.020	0.085	0.199

I - too intense to measure

4

Table 2

Intensity Measurements (Absorbance Units) of Probable iso-C_3F_7 Bands

Band	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z	aa	bb	cc
Expt. Frequency (cm⁻¹)	1365	1362	1249	1242	1206	1192	1157	1152	1141	1138	986	968	874	842	821	775	731	703	684	613	543	499	489	456	347	321	293	255	207
17	0.096	0.090	0.121	0.136	0.156	0.039	0.134	0.106	0.007	0.029	0.137	0	0	0	0	0	weak	0.062	0	0	0.0233	-	0	0	-	0	0	-	-
22	0.411	0.391	0.458	0.564	0.597	0.167	0.519	0.396	0.027	0.111	0.533	0.0073	0.0044	0	0	0.0051	0.0080	0.239	0.0075	0.033	0.0782	0.0231	0.022	0.0123	0	0	0.0056	-	-
23	-	-	-	-	-	0.678	-	-	0.215	0.454	1	0.0142	0.0118	weak	0.0044	0.0287	0.0412	1	0.0346	0.0125	0.168	0.0335	0.035	0.0538	0	0	0.0229	0	0
24	-	-	-	-	-	-	-	0.182	-	1	1	0.0398	0.0289	0.0066	0.0095	0.0555	0.0877	1	0.0676	0.0211	-	-	weak	0.101	-	-	0.0363	0	0
25	0.331	0.310	0.381	0.438	0.491	0.132	0.417	0.301	0.018	0.034	0.420	0.0063	0	0	0	0.0065	0.0075	0.188	0.0040	0.019	0.0162	0	weak	0.0101	0	0	0.0041	-	-
26	0.428	0.404	0.537	0.562	0.638	0.181	0.551	0.421	0.031	0.121	0.559	0.0056	0.0033	0	0	0.0051	0.0091	0.258	0.0069	0.026	0.0181	weak	0	0.0131	0	0	-	0	0
27	0.340	0.350	0.630	0.465	0.543	0.129	0.429	0.316	0.025	0.0267	0.433	0.0070	weak	0	0	0	0.0091	0.213	0.0080	weak	0.0161	0	-	0.0106	0.0162	0.017	0.0540	-	-
28	-	-	-	-	-	-	-	-	-	-	1	0.0647	0.0537	0.0106	0.0106	0.104	0.158	1	0.143	0.0514	0.486	0.0486	0.047	0.167	0.0316	0.0251	0.104	0.056	-
29	-	-	-	-	-	-	-	-	-	-	-	0.0908	0.102	0.0206	0.0327	0.171	0.317	1	0.243	0.118	1	0.0870	0.082	0.286	0.0409	0.0403	0.148	0.070	0.049
30	-	-	-	-	-	-	-	-	-	-	-	0.149	0.149	0.0306	0.0496	0.268	0.552	1	0.361	0.152	1	0.129	0.120	0.412	0.075	0.060	0.239	0.098	0.111
33	-	-	-	-	-	-	-	-	-	-	1	0.239	0.265	0.061	0.085	0.426	1	1	0.806	0.347	1	0.176	0.176	0.703				0.215	0.187

I - too intense to measure

compounds. This assumption is so made here. Little is known of the stability of the resulting perfluoro-radicals. Kinetic data on the two reactions, $CF_3CF_2\dot{C}F_2 \rightarrow \dot{C}F_3 + CF_2{=}CF_2$ or $CF_3\dot{C}F_2 + \dot{C}F_2$ have recently been reviewed [5] indicating both channels of equal importance at $\simeq 700K$, with higher temperatures favoring the latter mode. Kinetic data on the decomposition of iso-C_3F_7 does not appear to be available.

In the present study both CF_3 and C_2F_4 were identified as major side products in the pyrolysis of n-C_3F_7I, but no CF_3CF_2 as the above kinetic data suggests. Although CF_2 was found, which could be taken as evidence for the second reaction it should be noted that under these experimental conditions the pyrolysis of CF_3I always resulted in the formation of some CF_2 presumably due to partial decomposition of CF_3[1,2]. C_3F_6 was a minor product in the pyrolysis and presumably could be formed by F-atom elimination from the radical on the effusion tube surface. The present finding that C_3F_6, C_2F_4, CF_3 and CF_2 are major side products in the pyrolysis of iso-C_3F_7I suggest that both fluorine atom elimination and migration occur readily if these products are to be accounted for. It is possible on pyrolysis that in addition to simple C-I fission, a concerted elimination reaction could take place, with IF being eliminated and C_3F_6 formed; this type of behavior is known to occur in the pyrolysis of same alkyl halides with hydrogen halide being eliminated.[6] However, in the present study no evidence for the formation of IF was obtained from the recorded spectra,[7] ν (IF) $\simeq 604$ cm^{-1}.

In light of the above, it appears reasonable to conclude that the majority of the unknown absorption bonds listed in Table 3 and 4 may be assigned to the perfluoro-n- and iso-propyl radicals. As noted in a previous paper[1] in view of the experimental difficulties the errors on the intensity correlations given in Table 4 are consistent with assignment of all the absorption bands to a single species, iso-C_3F_7. The intensity correlation data for n-C_3F_7 in Table 3 are not nearly so comprehensive due to absorption band overlap problems, though where values were calculated the agreement is acceptable.

Table 3

Relative Intensity Ratios For Probable n-C$_3$F$_7$ Bands

Band	Frequency (cm^{-1})	Intensity Correlation With Band at 1016 cm^{-1}	Intensity Correlation With Band at 638 cm^{-1}	Remarks
a	1354 (m)	?	?	overlapped with C$_3$F$_7$I band
b	1287 (vs)	± 7.2%	± 9.9%	partially overlapped with band c
c	1285 (vs)	± 9.2%	± 10.0%	partially overlapped with band b
d	1260 (m)	?	?	overlapped with C$_3$F$_7$I band
e	1236 (s)	?	?	partially overlapped with C$_3$F$_7$I band and band f
f	1231 (s)	?	?	partially overlapped with C$_3$F$_7$I band and band e
g	1222 (vs)	?	?	overlapped with C$_3$F$_7$I band
h	1191 (s)	?	?	overlapped with C$_3$F$_7$I band
i	1185 (w)	?	?	overlapped with C$_3$F$_7$I band
j	1121 (m)	?	?	overlapped with C$_3$F$_7$I band
k	1116 (s)	± 7.7%	± 1.8%	partially overlapped with bands j and l
l	1114 (s)	± 9.7%	± 10.5%	partially overlapped with band k
m	1034 (w)	?	?	overlapped with C$_3$F$_7$I band
n	1016 (m)	reference	± 3.3%	
o	958 (vw)	± 28.7%	± 36.7%	overlapped with weak C$_3$F$_7$I band
p	888 (m)	?	?	overlapped with C$_3$F$_7$I band
q	750 (m)	?	?	overlapped with C$_3$F$_7$I band
r	703 (w)	?	?	overlapped with CF$_3$ band
s	638 (m)	± 3.3%	reference	
t	621 (w)	?	?	overlapped with C$_3$F$_7$I band
u	608 (vw)	± 18.4%	± 16.5%	
v	562 (vw)	± 12.7%	± 32.1%	overlapped with weak C$_3$F$_7$I band
w	549 (w)	± 23.6%	± 16.4%	overlapped with weak C$_3$F$_7$I band
x	520 (w)	± 20.5%	± 22.8%	
y	472 (vw)	too weak to correlate	± 13.4%	overlapped with weak C$_3$F$_7$I band
z	465 (vw)	too weak to correlate	± 16.0%	overlapped with weak C$_3$F$_7$I band
aa	401 (vvw)	too weak to correlate	± 17.4%	
bb	395 (vvw)	too weak to correlate	± 2.8%	
cc	306 (w)	too weak to correlate	± 24.8%	overlapped with weak C$_3$F$_7$I band
dd	273 (w)	± 2.3%	± 18.0%	overlapped with weak C$_3$F$_7$I band
ee	265 (vvw)	?	?	insufficient information for correlation test
ff	248 (vw)	?	?	insufficient information for correlation test
gg	220 (vw)	?	?	insufficient information for correlation test

Table 4

Relative Intensity Ratios For Probable iso-C_3F_7 Bands

Band	Frequency (cm⁻¹)	Intensity Correlation With Band at 986 cm⁻¹	Intensity Correlation With Band at 456 cm⁻¹	Remarks
a	1365 (s)	± 5.0%	± 1.7%	partially overlapped with band b
b	1362 (s)	± 7.6%	± 3.0%	partially overlapped with band a
c	1249 (vs)	± 18.7%	± 24.0%	partially overlapped with CF₃ band, iso-C₃F₇I band and band d
d	1242 (vs)	± 3.3%	± 3.0%	partially overlapped with band c
e	1206 (vs)	± 4.2%	± 2.7%	
f	1192 (m)	± 5.1%	± 5.2%	
g	1157 (vs)	± 0.9%	± 1.7%	partially overlapped with band h
h	1152 (s)	± 3.1%	± 4.4%	partially overlapped with band g
i	1141 (w)	± 11.9%	± 33.8%	partially overlapped with band j
j	1138 (m)	± 3.5%	± 5.4%	partially overlapped with band i
k	986 (vs)	reference	± 2.6%	reference band for intensity correlation
l	968 (vw)	± 22.5%	± 31.7%	
m	874 (vw)	± 23.5%	± 18.5%	
n	842 (vvw)	too weak to correlate	± 13.1%	overlapped with iso-C₃F₇I band
o	821 (vvw)	too weak to correlate	± 23.7%	overlapped with iso-C₃F₇I band
p	775 (w)	± 26.5%	± 17.3%	
q	731 (w)	± 14.1%	± 24.9%	overlapped with iso-C₃F₇I band
r	703 (m)	± 3.9%	± 3.2%	
s	684 (w)	± 27.3%	± 28.9%	overlapped with iso-C₃F₇I band
t	613 (vw)	± 16.5%	large	overlapped with iso-C₃F₇I band
u	543 (w)	± 10.9%	± 29.8%	overlapped with iso-C₃F₇I band
v	499 (vw)	too weak	± 19.1%	
w	489 (vw)	too weak	± 18.6%	
x	456 (w)	± 2.6%	reference	reference band for intensity correlation
y	347 (vvw)	too weak	± 6.0%	
z	321 (vvw)	too weak	± 8.6%	
aa	293 (vw)	± 5.2%	± 12.7%	
bb	255 (vw)	too weak	± 17.9%	
cc	207 (vw)	too weak	± 6.7%	overlapped with iso-C₃F₇I band

Tentative frequency assignments for n-C_3F_7 iso-C_3F_7 are presented in Table 5 and 6 using the frequencies listed in Tables 3 and 4, respectively. In making these frequency assignments, comparable vibrational assignments for C_3F_8[8,9] and C_3F_7I[8,10] were used as models. Both n-and iso-C_3F_7 radicals could exist with either C_1 or C_s symmetry. In the C_s configuration, two rotational conformers are possible for both radicals. In the C_1 configuration, only for n-C_3F_7 are two rotational conformers possible. Obviously the present data do not permit resolution of any of these possibilities. In all cases, a total of 24 IR active frequencies would be expected. Two torsional modes and C-C-C skeletal bend[9] for both radicals almost certainly lie above 50 μ, the long wave length limit of the present study leaving a total of 21 frequencies which potantially could be observed in the present study. C_s symmetry was arbitrarily assumed for the purpose of making the assignments given in Tables 5 and 6. For the iso-radical, frequencies of similar vibrational modes in C_3F_8[9] are presented for comparison.

For both radical species it was necessary to assume that some of the high frequency C-F stretching mode absorption bands in the 1100-1400 cm^{-1} region; occurred as doublets. Only seven frequencies in this region are expected; yet for both radicals, ten maxima were identified. The appearance of some of these bands as doublets could be due to matrix site effects or could be a manifestation of the existence of two different structural forms, C_s or C_1 or their rotational conformers. In either case it would be reasonable to expect some of the lower frequency modes might also occur as doublets, and, although not specifically indicated in Tables 2 and 3, some indeed did. Thus, in the iso-C_3F_7 spectrum the bands labelled p and bb are quite broad possibly indicating the presence of closely lying doublets whilst the band g appears to have a doublet structure.

Only one CF_3 stretching frequency above 1300 cm^{-1} occurs in CF_3CF_2[a] suggesting that a similar situation in n-C_3F_7 is not unreasonable. The situation for iso-C_3F_7 is not so clear cut. In C_3F_8,[9] three CF_3 stretching vibrations over 1300 cm^{-1} were assigned whilst in CF_3COCF_3[a], only one. In the assignment presented in Table 6 for iso-C_3F_7, a probable doublet at

Table 5

TENTATIVE FREQUENCY ASSIGNMENT FOR n-C_3F_7 OF C_S SYMMETRY

α' Modes	Observed Frequency (cm^{-1})	Approximate Mode Description
ν_1	1354	ν_s CF_3
ν_2	1287-1285	ν_{as} CF_3
ν_3	1236-1231	ν_s CF_2
ν_4	1222	ν_{as} CF_2
ν_5	1016	ν_{as} CC_2
ν_6	750	δ_s CF_3
ν_7	683	δ_{as} CF_3
ν_8	608	δ CF_2
ν_9	548	δ CF_2
ν_{10}	520	δ CF_2
ν_{11}	465	δ CF_2
ν_{12}	273	δ CF_2
ν_{13}	306	ν_s CC_2
ν_{14}	220	ρ CF_3
ν_{15}	--	δ CC_2
α' Modes		
ν_{15}	1260	δ CC_2
ν_{16}	1191	ν_{as} CF_3
ν_{17}	1116-1114	ν_{as} CF_2
ν_{18}	703	ν_{as} CF_2
ν_{19}	621	ν_{as} CF_3
ν_{20}	472	ρ CF_2
ν_{21}	248	ρ CF_2
ν_{22}	--	ρ CF_3
ν_{23}	--	torsion
ν_{24}	--	torsion

ν_s = Symmetric stretching ν_{as} = Asymmetric stretching

ν_s = Symmetric deformation δ_{as} = Asymmetric deformation

ν = Stretching ρ = rocking δ = bending

Table 6

TENTATIVE FREQUENCY ASSIGNMENT FOR Iso-C_3F_7 OF C_S SYMMETRY

	Observed Frequency (cm^{-1})	Approximate Mode Description	
α' Modes			
ν_1	1365-1362	ν_s CF$_3$	1370[a]
ν_2	1242	ν_s CF$_3$	1350
ν_3	1192	ν_{as} CF$_3$	1262
ν_4	1157-1152	ν_{as} CF$_3$	1210
ν_5	1141-1138	ν_s CF	
ν_6	986	ν_{as} CC$_2$	1007
ν_7	775	δ_s CF$_3$	781
ν_8	731	δ_s CF$_3$	731
ν_9	703	δ CCF	337
ν_{10}	499	δ_{as} CF$_3$	548
ν_{11}	489	δ_{as} CF$_3$	507
ν_{12}	347	ρ CF$_3$	383
ν_{13}	321	ν_s CC$_2$	318
ν_{14}	293	ρ CF$_3$	278
ν_{15}	--	δ CC$_2$	151
α'' Modes			
ν_{16}	1249	ν_{as} CF$_3$	1370
ν_{17}	1206	ν_{as} CF$_3$	1268
ν_{18}	684	δ_{as} CF$_3$	618
ν_{19}	543	δ_{as} CF$_3$	537
ν_{20}	456	ρ CF$_3$	461
ν_{21}	255	ρ CF$_3$	276
ν_{22}	207	δ CCF	219
ν_{23}	--	torsion	--
ν_{24}	--	torsion	--

ν_s = Symmetric stretching ν_{as} = Asymmetric stretching

δ_s = Symmetric deformation δ_{as} = asymmetric deformation

ν = stretching ρ = rocking δ = bending

[a] Analogous frequencies of $CF_3CF_2CF_3$.

1365-1362 cm^{-1} is the only frequency greater than 1300 cm^{-1} assigned to a CF$_3$ stretching mode. It is entirely possible that the doublet is in reality two distinct frequencies assignable to two different CF$_3$ stretching modes, perhaps, ν_1 and ν_{16} and that ν_2 appears as a doublet at 1242-1249 cm^{-1}.

The asymmetric carbon skeletal stretching mode is expected with moderate intensity at about 1000 cm^{-1}[8,9]. Bands at 986 and 1016 cm^{-1} appearing in Figures 2 and 4 are thus assigned to carbon skeletal stretching modes in iso-C$_3$F$_7$ and n-C$_3$F$_7$ respectively. Assignment of the remaining absorption bands to the various bending deformation and rocking modes for both radicals is at best somewhat arbitrary, though reasonable by comparison with other assignments in similar molecules. Obviously not all the frequencies listed in Tables 3 and 4 have been used in the present vibrational assignments for each of the radicals. The "excess" frequencies can be accounted for in terms of combination, difference or overtone modes but the possibility that some of these frequencies could be assigned more properly to different conformers of the radicals cannot be eliminated.

In the present study the spectral region below 200 cm^{-1} was not examined and hence two expected torsional modes and a carbon skeletal bend for each radical in this region were not observed. In C$_3$F$_8$ the magnitude of torsional modes are also not known. Excluding torsional modes, the vibrational assignment now available for the fluorine radicals CF$_2$,[11] CF$_3$,[12] C$_2$F$_5$[2], n-C$_3$F$_7$ and iso-C$_3$F$_7$ strongly suggest that the magnitudes of the radical vibration frequencies could be estimated[4] without serious error from the values of those occurring in analogous saturated compounds. EPR studies on perfluoro radicals indicate that the tetrahedral geometry of the carbon atom at the radical center is maintained. These two findings suggest that fairly good confidence can be placed in thermodynamic data, S$^\circ$ and C$^\circ_p$ estimated for the perfluoro-alkane radicals based on structural and energy level data[4] derived from saturated analogues. Two areas of uncertainty remain in such estimations for the larger radicals, 1) are the torsional modes much different in the perfluoro-radicals as compared to the saturated compounds, and 2) do the radicals exist in more than one structural form?

By extending the present matrix method to longer wavelenghts the torsional modes could be observed, but it appears unlikely that differentiation of structural conformers could be achieved.

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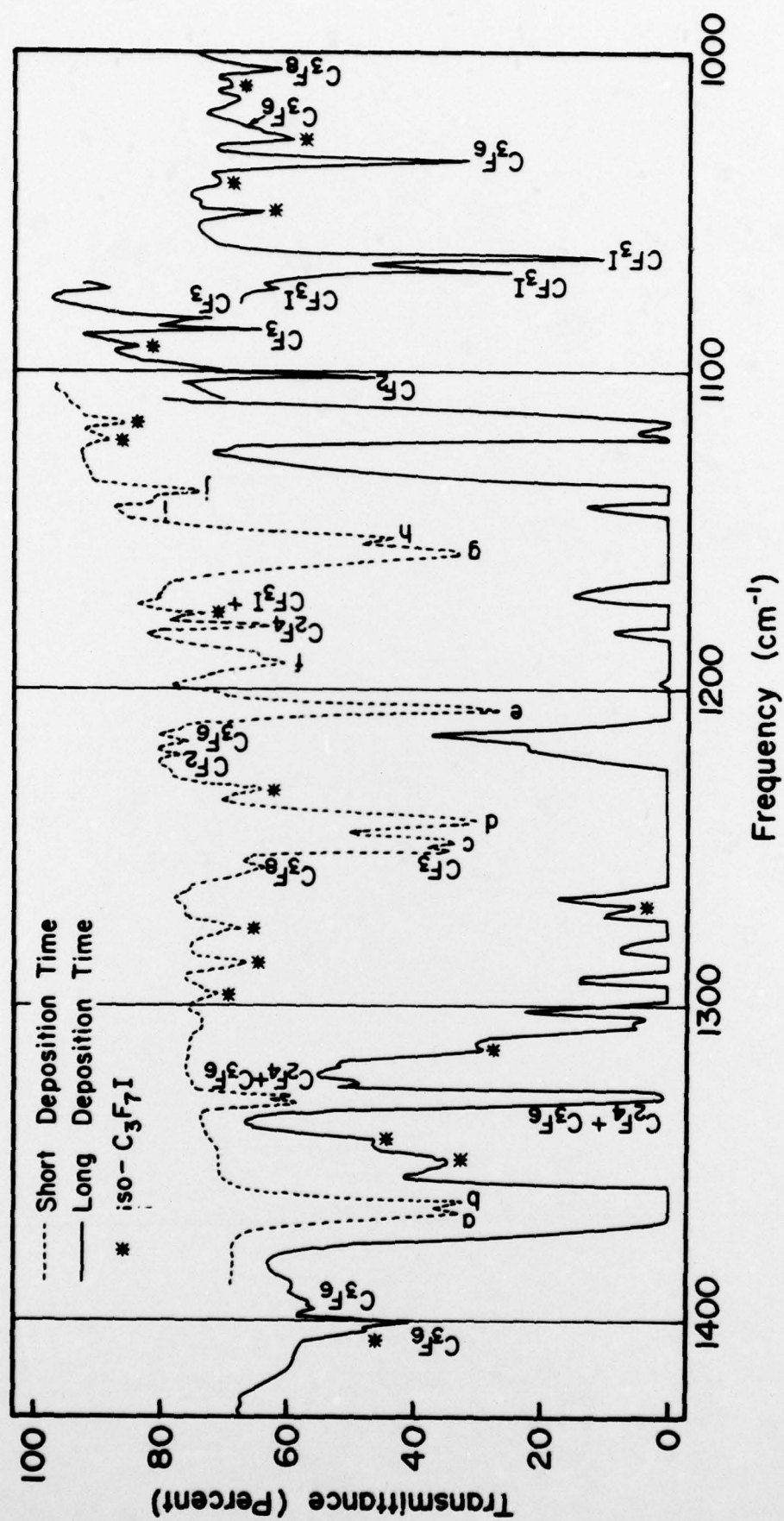
Fig. 1 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF iso-C_3F_7I

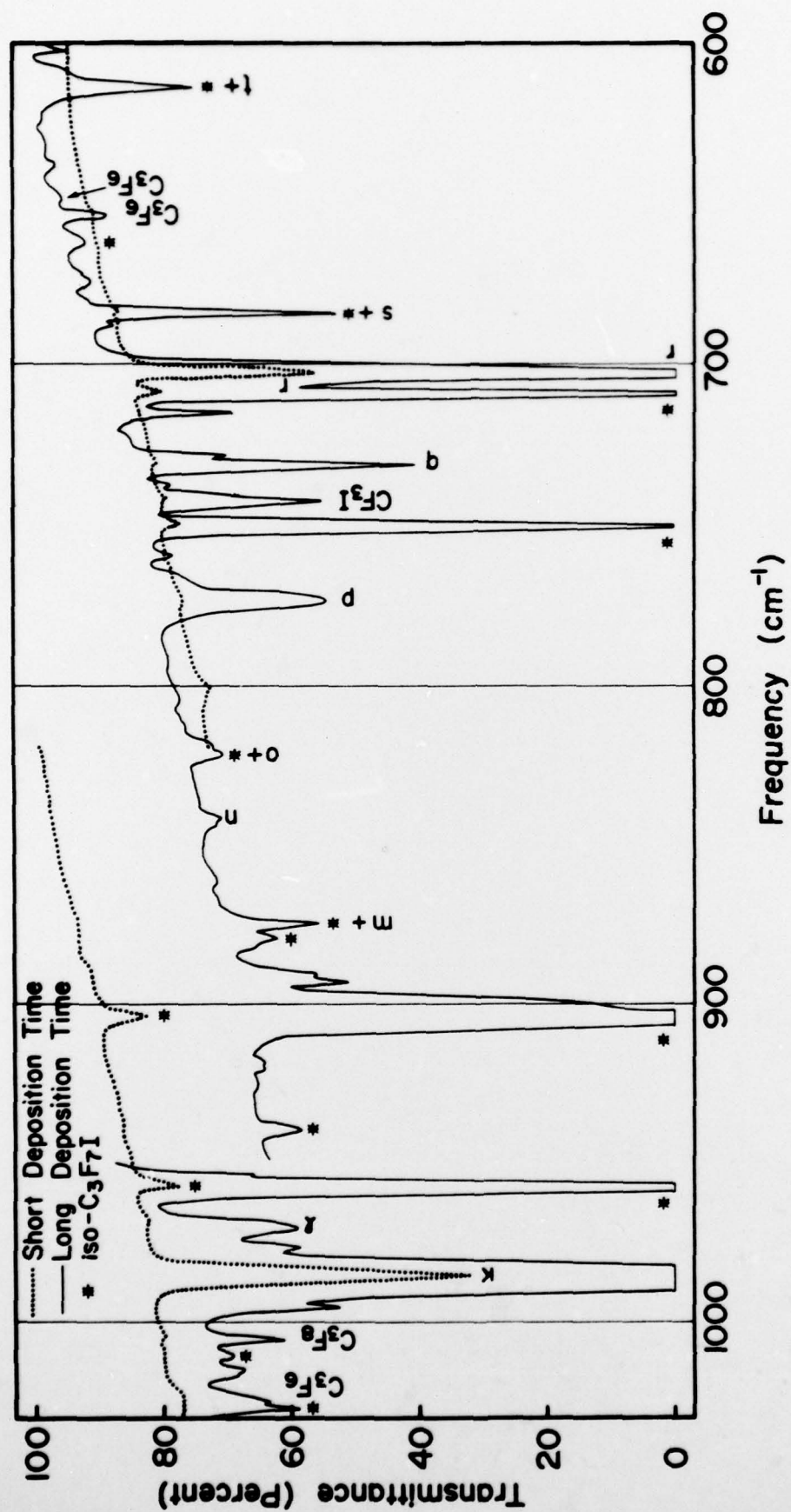Fig. 2 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF iso-C_3F_7I

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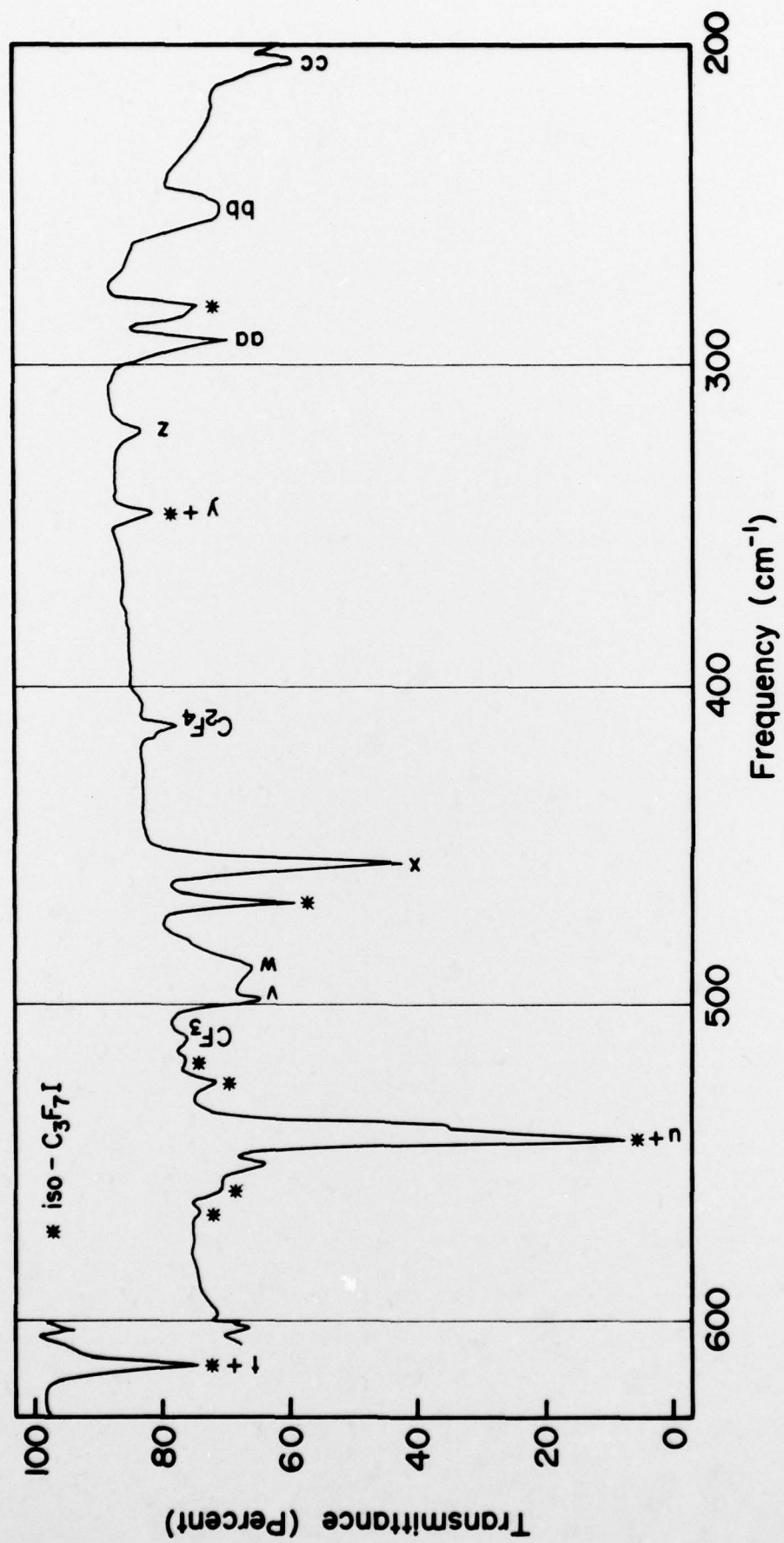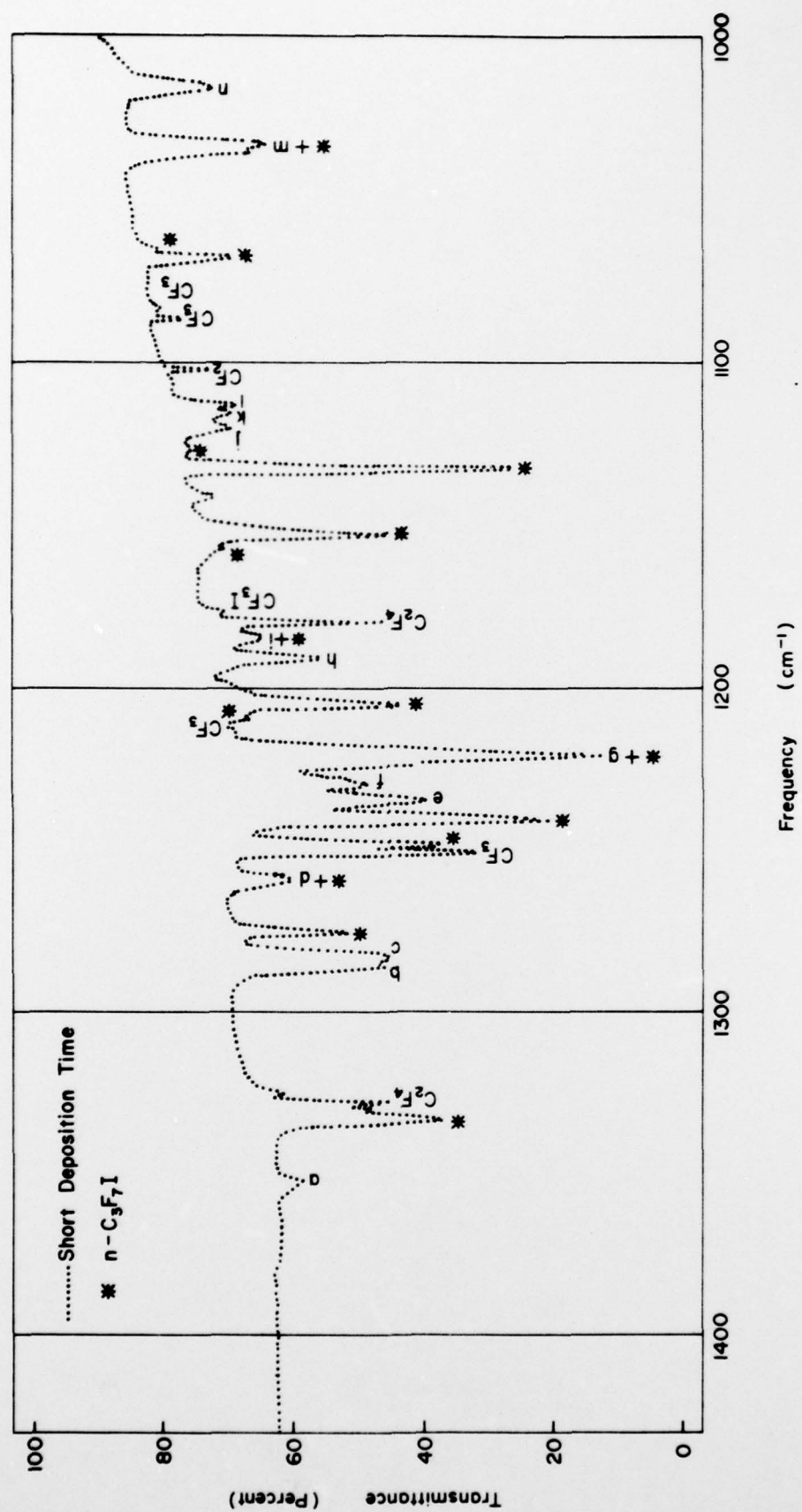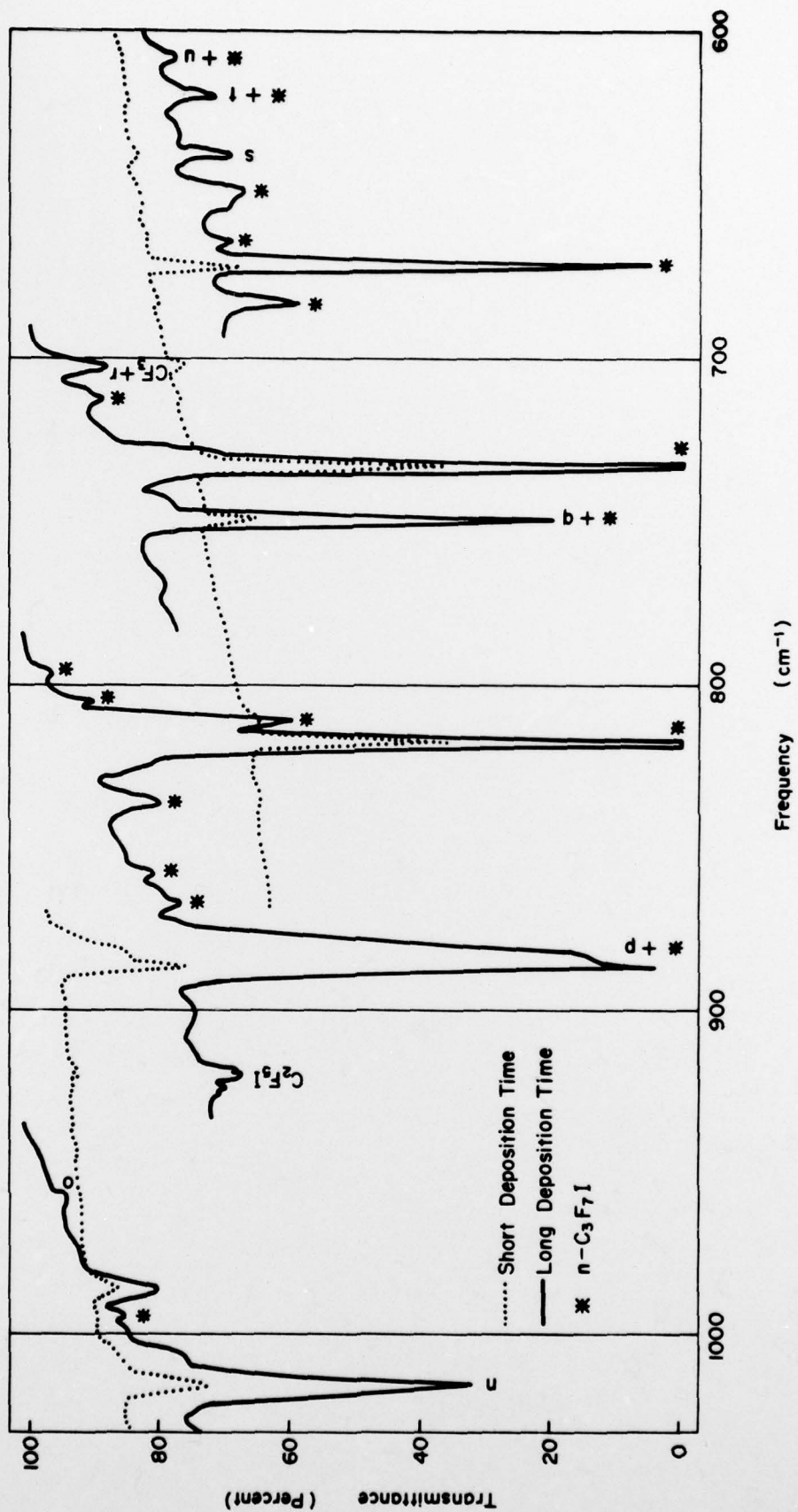
Fig. 3 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF iso-C_3F_7I

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Fig. 4 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF n-C₃F₇I

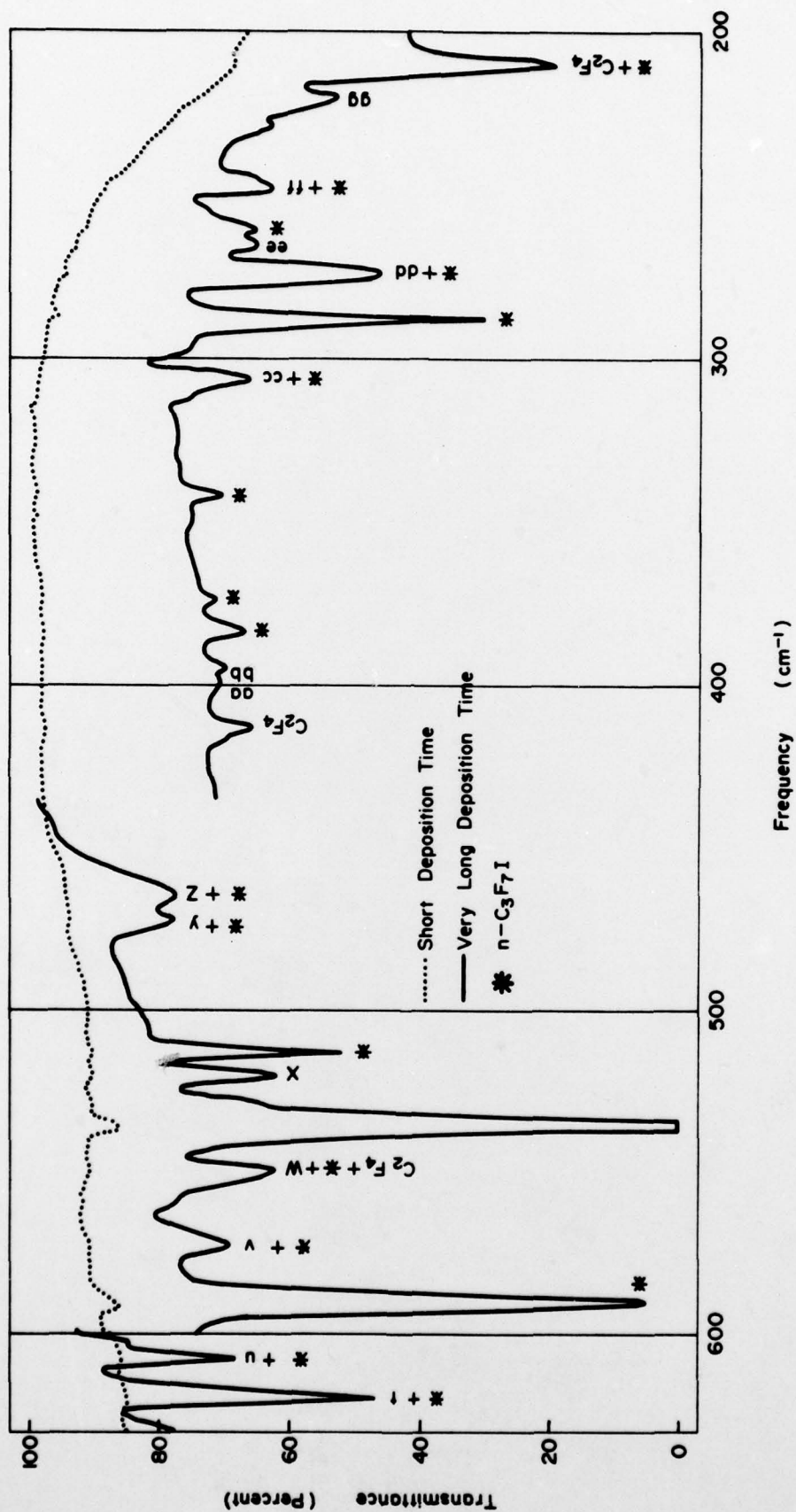Fig. 5 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF n–C₃F₇I

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Fig. 6 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF n–C$_3$F$_7$I

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SHORT COMMUNICATION

IR Matrix Isolation Product Characterization from
Low-Pressure Pyrolysis of $C_nF_{2n+1}I$ (n = 1-4) and C_6F_5I

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Studies directed at characterizing the IR matrix isolation spectra of the perfluoro-radicals--CF_3 [1], CF_3O_2 [2], C_2F_5 [3], n-C_3F_7 [4], and iso-C_3F_7 [4] --have recently been described. Some observations are presented here on the pyrolysis behavior of the perfluoro-alkyl iodides CF_3I, C_2F_5I, n-C_3F_7I, and iso-C_3F_7I, which were successfully used to produce the corresponding perfluoro-alkyl radicals, and also on the pyrolysis behavior of t-C_4F_9I and C_6F_5I, which did not produce the expected t-C_4F_9 and C_6F_5 radicals.

In the matrix isolation experiments, the perfluoro-alkyl iodides were decomposed in a very low-pressure (reactant pressure $\approx 10^2$ Pa) platinum pyrolysis reactor. Under the conditions used, reactor residence time was $\approx 3.4 \times 10^{-3}$ sec, with each molecule on average undergoing 10 wall collisions. Gas molecule-molecule collisions were about one hundredth of the wall rate. Under such conditions, the contribution of gas phase collisions to the overall reaction process may be ignored. The C_1, C_2, and C_3 perfluoro-alkyl iodides all showed substantial decomposition (30-80%) in the 900-700K temperature range, with somewhat lower average temperatures being required to obtain a given decomposition fraction in the order $C_1 > C_2 > C_3$. This finding is consistent with a recent determination of C—I bond energies [5] in CF_3I (222.6 kJ mol^{-1}), C_2F_5 (216.2 kJ mol^{-1}), and n- and iso-C_3F_7I (208.4 kJ mol^{-1}), assuming the primary process is simple C—I bond fission. In all these experiments there were moderate amounts of other products formed besides the respective radicals.

The pyrolysis of CF_3I always resulted in the formation of CF_3, CF_4, CF_2, and C_2F_6. Assuming that extinction coefficients for the C—F stretching modes of all four species are similar, their relative amounts may be estimated at $1 : 0.47 : 0.24 : 0.11$ from data in a typical experiment. The presence of C_2F_6 could perhaps be justified in terms of incomplete isolation during the trapping process, allowing the reaction $CF_3 + CF_3 \rightarrow C_2F_6$ to occur. The activation

energy for this radical recombination is known to be close to zero. Indeed, the relative amount of $CF_3 : C_2F_6$ did show a marked sensitivity to matrix dilution, the ratio increasing noticeably as the dilution, and hence trapping efficiency, increased. This type of behavior was not shown by either CF_4 or CF_2 with respect to CF_3. Furthermore, when CF_3 radicals were isolated in argon matrices containing 5-20% O_2 [2], no C_2F_6 was ever identified even though small amounts of unreacted CF_3 were always present. CF_4 and CF_2 were present to the degree normally associated with a pure argon matrix. These observations strongly suggest that the reaction $CF_3 + CF_3 \rightarrow CF_4 + CF_2$, which is exothermic by $\approx$-182.4 kJ mol^{-1} [7], does no occur in the matrix. Indeed, there does not appear to be any experimental evidence that at ambient or elevated temperatures [6] such a reaction channel exists. The conclusion seems inescapable that CF_4 and CF_2 must be formed heterogeneously on the walls of the platinum reactor. This conclusion is further reinforced by the observation that the amounts of CF_4 and CF_2 formed relative to CF_3 could be decreased by reducing the CF_3I pressure in the reactor during pyrolysis.

In the pyrolysis of C_2F_5I [3] to produce C_2F_5, small amounts of CF_3, CF_2, and possibly C_2F_4 were formed, the amounts of CF_3 and CF_2 clearly increasing with respect to C_2F_5 at higher pyrolysis temperatures. Thermodynamic data [7] indicate a minimum activation energy for the homogeneous gas phase reaction $C_2F_5 \rightarrow CF_3 + CF_2$ at 326.4 kJ mol^{-1}, strongly suggesting this reaction is not important under our experimental conditions. Minimal activation energy for the gas phase reaction $C_2F_5 \rightarrow C_2F_4 + F$ [7,8], estimated at 316.3 kJ mol^{-1}, also eliminates this as a likely reaction. Again, the radical product distribution implies heterogeneous surface effects are important.

Pyrolysis of n- and iso-C_3F_7I produced the desired radicals and fairly substantial amounts of C_2F_4, CF_3, CF_2, and C_3F_6, C_2F_4, CF_3, and CF_2, respectively. Obviously C—C and C—F bond breaking occurred. Thermochemical data are not well defined for the perfluoro-propyl radicals and implication of surface effects cannot be invoked on this basis. The radical C_2F_5 was not detected in the pyrolysis of n-C_3F_2I though some recent thermochemical-kinetic data [7] suggest that the reaction n-$C_3F_7 \rightarrow C_2F_5 + CF_2$ takes place at temperatures used in the study.

The pyrolysis of t-C_4F_9I [9] was performed initially in the 900-700K temperature range with the other experimental conditions identical to that used with the lower homologues. Complete decomposition of t-C_4F_9I to $(CF_3)_2C=CF_2$ occurred. The latter material was unequivocally identified by

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comparison with the matrix spectrum of the pure compound [9]. At 575K, about 50% decomposition of the parent iodide occurred, with only one product, $(CF_3)_2C=CF_2$ identified at short deposition times ($\simeq 1$ hr). At longer deposition times (4-5 hr), a very weak absorption band at 603 cm^{-1} also became apparent in addition to those expected for t-C_4F_9I and iso-C_4F_8. Experimental identification of the feature at 603 cm^{-1} was not pursued, though an obvious possibility would be IF. The latter's gas phase vibration frequency has been reported [10] at 604 cm^{-1}. In this connection an effort was made to determine if the matrix did contain free fluorine atoms, possibly formed by elimination from t-C_4F_9 in the pyrolysis tube, which could lead to IF formation by matrix reactions between F and I atoms. To this end t-C_4F_9I was pyrolyzed into argon matrices containing 5% O_2 or 5% CO. If F-atoms were being injected into the matrix, previous work in this laboratory and elsewhere has shown that FO_2 or FCO would readily be formed [11,12]. In the present investigation, no FO_2 or FCO could be detected and the absorption band at 603 cm^{-1} remained. If indeed this feature were correctly assignable to FI, the latter must have originated in the pyrolysis tube and not from a matrix reaction between F and I atoms.

That no t-C_4F_9 radical was found on pyrolysis of C_4F_9I may indicate that C—I bond fission is not the primary process in this system. The close similarity in C—I bond energies in the lower alkyl iodides (C_1 through C_3) with the analogous perfluoro-alkyl iodides [5] suggests that the C—I dissociation energy in t-C_4F_7I is probably a little less than in C_3F_7I, possibly by $\simeq 8 - 12$ kJ mol^{-1}, which seems insufficient to account for the markedly lower pyrolysis temperature required for this compound. Again it appears necessary to invoke surface effects in the pyrolysis process with the possible formation of the perfluoro-butene, occuring via a concerted four center elimination reaction analogous to that occurring in the pyrolysis of some alkyl iodides [13]. A minimum activation energy for the latter process, ignoring surface effects, may be crudely estimated from C—F, C—I, and I—F bond dissociation energies of 456, 193, and 277 kJ mol^{-1}, and a π bond stabilization energy of 222 kJ mol^{-1} [14], at 150 kJ mol^{-1} a value which, with perhaps some surface assistance, is not inconsistent with the low pyrolysis temperature observed.

The pyrolysis of C_6F_5I required temperatures of 1000-1100K to obtain substantial decomposition, some 100-200K higher than in the C_1—C_3 perfluoro iodides, a finding consistent with C—I bond dissociation in C_6F_5I at 277 kJ mol^{-1} [15]. This latter value was determined using the toluene carrier gas technique. The presence of the C_6F_5 radical in the system was inferred from the formation of

C_6F_5H by H abstraction from the toluene carrier gas. In the matrix study the only products found on pyrolysis of C_6F_5I were unreacted C_6F_5I, CF_4, CF_3, and CF_2 in approximately equal amounts. No evidence of absorption features attributable to any other species was found. These results imply a complete breakdown of the benzenoid ring structure on pyrolysis. When the pyrolysis products were trapped in an argon matrix containing 5% O_2, CF_3O_2 [2] was immediately recognizable in the product spectrum. No FO_2 was found, indicating the absence of free F-atoms in the pyrolysis reaction; nor was there any trace of COF_2, invariably found when CF_3, formed by the pyrolysis of CF_3I, was allowed to react with an oxygen-doped matrix in an earlier study [2]. Substantial amounts of CO and CO_2 were found; whether their formation occurred in the pyrolysis tube (by possible diffusion of O_2 into the pyrolysis zone) or by reaction of some carbon fragment in the matrix is not clear.

A few observations with respect to the overall pyrolysis behavior of these compounds will be noted. At the low pressures used in these studies, the activation energy for thermal decomposition is acquired solely by reactor-wall substrate interactions. The unimolecular reaction rate is expected to be well into the low-pressure fall-off region, yet the temperatures required to bring about substantial decomposition were about the same as would be required if the reaction were occurring at its high-pressure limit, assuming a normal Arrhenius factor [13] of $10^{16 \pm 1}$ and a C—I bond dissociation energy at ≈ 210 kJ mol^{-1}. In contrast, experiments to dissociate CH_3I in the same reactor to produce CH_3 radicals required a temperature of about 1300-1400K to obtain a similar degree of decomposition, indicating the reaction was behaving "normally" and in its low-pressure fall-off region. The perfluoro-iodides must undergo relatively "sticky" collision with the platinum surface with very efficient energy transfer, though for what reason is not clear. The dipole moments of both compounds are similar [17], $CH_3I \approx 1.6D$ and $CF_3I \approx 1.0D$, with the difference in the wrong direction to invoke dipole-surface interactions as of importance. Possibly, the marked positive electron affinities of the perfluoro compounds [18,19] compared to their hydrogenated analogues may be connected with the strong surface interaction [20].

Another factor that may affect the overall product distribution after initial scission of the C—I bond is the possible formation of a weakly bound Pt—F species. It has been shown [18] that F-atoms at low pressure (≈ 1Pa) will attack platinum in the 800-1100K region, though the nature of the resulting species was not identified.

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Finally, a possible advantage of the matrix isolation technique with respect to identifying the products of pyrolysis reactions influenced by surfaces is the unambiguous nature of the "IR fingerprint" of the product species. This is particularly valuable for identifying radicals in the presence of the parent molecule. The most widely used conventional approach to this analytical task is mass spectrometry, where radical detection is often conceded to be extremely difficult and sometimes impossible in the presence of the parent species.

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The pyrolysis of some perfluoro organic iodides have been used to prepare free radical species, of possible importance in flame inhibition chemistry, for infrared matrix isolation studies. The species CF_3O_2, C_2F_5, $n-C_3F_7$ and iso-C_3F_7 were identified and vibrational assignments made. For CF_3O_2, oxygen isotope studies were used to help in the vibrational assignments. Papers for publication have been prepared describing this work and are included in this report. Normal coordinate analyses for CF_3O_2 and C_2F_5 are currently in progress and will be

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submitted for publication in 1980. Preliminary data from these calculations strongly support the initial vibrational assignments made for $CF_3O_2^-$ and $C_2F_5^-$. Attempts were made to identify the species CF_3O, $t\text{-}C_4F_9^-$, $C_6F_5^-$ and $C_6F_5O_2^-$. Some evidence for the existence of CF_3O was found but was not definitive. The results of these latter studies are described in the first section of this report.